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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

## General and Physical Chemistry.

**Refraction of Light and Atomic Structure. Refraction Equivalents of Ions.** JARL A. WASASTJERNA (*Öfvers. Finska Vet.-Soc.*, 1921, **63**, [*A*], No. 4, 18 pp.; from *Chem. Zentr.*, 1921, iii, 759).—Cuthbertson's rule for the relation between the refraction equivalents of atoms and their position in the periodic system is applicable to the refraction equivalents of the ions of the alkali and alkaline-earth metals. It follows that the outer electron sheath of an alkali metal contains only one electron which in salt formation passes over to the acid half, which thereby becomes negative. In the case of alkaline-earth metals the outer sheath contains two electrons which go over to the negative atom or group. The next sheath in the alkali and alkaline-earth metals is identical with that in the preceding member of the horizontal series which is nearer to the nucleus on account of increased attraction. Numerical values are given for the refraction equivalent of positive and negative ions. G. W. R.

**The Molecular Refraction of Substances of Higher Melting ... Calculation of the Corresponding Refractive ... the Temperature of Comparison, 20°.** FRITZ ... 1921, **54**, [*B*], 2857—2867).—Difficulties are ...ating the refractive values of substances of ... above 20°, since values calculated from the

Lorentz-Lorenz expression increase perceptibly with increasing temperature, whereas those calculated according to Gladstone-Dale decrease to about a corresponding extent. The only expression for the molecular refraction which is nearly independent of the temperature is that of Eykman, $(n^2-1)M/(n+0{\cdot}4)d$, but this has never become popular with chemists. If $a$ and $b$ are the factors for the conversion of the Lorentz-Lorenz and Gladstone-Dale to the Eykman values, the expressions $n^2-1/n+0{\cdot}4=a(n^2-1)/(n^2+2)$ and $n^2-1/n+0{\cdot}4=b(n-1)$ are obtained, whence $a=n^2+2/n+0{\cdot}4$ and $b=n+1/n+0{\cdot}4$. For a given interval of temperature, for example 10°, it is found that the alteration in $\log a \times \log b$ is approximately constant and independent of the value of the refractive index; for the given temperature interval, $\log a=-0{\cdot}00033$ and $\log b=+0{\cdot}00024$. The latter value cannot be regarded as completely independent of the magnitude of the refractive index if this varies greatly from the normal value ($n=1{\cdot}45$) and, for this case, a modified table of corrections is given, but, in general, the values quoted are sufficiently accurate. A number of examples are quoted showing the method of calculating the refractive index from one temperature to another over considerable intervals of temperature; in general, the observed and calculated values are in excellent agreement, but cymene affords an exception. A small number of other substances also do not behave in accordance with Eykman's formula. The substances appear to have a very appreciable vapour tension at the atmospheric temperature and to pass at a comparatively low temperature into a region in which there is no longer a perfectly uniform change of refractive index with the temperature. For safety, it is advisable to restrict observations to a region which does not embrace more than one-third of the temperature of ebullition as usually expressed. H. W.

**Optical Properties of Solutions. A Theory of the Structure of the Molecules of Electrolytes.** JARL A. WASASTJERNA (*Acta Soc. Sci. Fennicae*, 1920, **50**, No. 2, 129 pp.; from *Chem. Zentr.*, 1921, iii, 758—759).—The refractive indices and densities of aqueous solutions of a number of organic salts, sodium chloride, potassium chloride, and oxalic acid were determined for two different temperatures and for three different wave-lengths at each temperature. From the results obtained certain conclusions were drawn as to the influence of dissociation on the optical properties of electrolytes. The number of valency electrons in each atom may be directly calculated from Eisenlohr's atomic refraction constant and the results are in agreement with Drude's valency theory. A new interpretation of the Lorenz-Planck dispersion formula is given leading to a working hypothesis whereby the selective photoelectric effect can be calculated as well as, in certain cases, the alteration in refraction and dispersion due to ionisation. It is shown that the temperature coefficient of molecular [illegible] for dissolved salts is always negative by the New[illegible] formula, variably positive and negative by the G[illegible] formula, and negative by the Lorentz-Lorenz f[illegible]

further shown that the additive character of specific refractive power is satisfied by the Gladstone-Dale formula. For the determination of the molecular refraction of dissolved salts, strong solutions should be used and the values extrapolated for 100%. The optical properties of salt solutions can be simply explained by assuming that the ions occur ready formed in solutions of strong electrolytes whilst the molecules of weak electrolytes cannot be thus polarised. G. W. R.

**Notes of Spectrography.** E. VON ANGERER (*Physikal. Z.*, 1921, **22**, 521—523).—A description of various modifications of apparatus and technique used by the author in spectroscopic work. The points included refer to (*a*) the iron arc, (*b*) the mercury reference spectrum, (*c*) the reproduction of a wave-length scale, and (*d*) an ultra-violet monochromatic light filter. J. F. S.

**The Origin of Band Spectra.** YUTAKA TAKAHASHI (*Proc. Phys. Math. Soc. Japan*, 1921, [3], **3**, 20—28, 30—33).—It is possible to deduce a formula representing a system of band spectra from the oscillation of the atoms in a molecule if, with Bohr and Sommerfeld, the quantum relations $A_1 - A_2 = h\nu$ and $\int_1 p_i\, dq_i = n_i h$ are accepted for the conditions of the radiation and the stationary state. A simple Deslandres formula $\nu = A + B(n_1^2 - n_2^2)$ where $B = h/8\pi^2 I_0$ is arrived at. If the angular momentum of the molecular rotation is not a complete multiple of $h/2\pi$ the formula becomes $\nu = A \pm B(n + \epsilon)^2$, where $\epsilon < 1$ as observed in many cases. The theoretical values of $A$ and $B$ in the last equation are found to be of the same order of magnitude as the observed ones for band spectra of nitrogen and oxygen. In the low potential discharge in hydrogen, Fulcher isolated two triplet bands. It is shown that these bands can be represented by the author's formula by taking suitable values for the constants. CHEMICAL ABSTRACTS.

**The Changeable Fine Structure of the Balmer Series.** E. GEHRCKE and E. LAU (*Physikal. Z.*, 1921, **22**, 556—557).—A change in pressure brings about a change in the intensity relationship of the two components of the Balmer series, which is a series of doublets. The intensity change is most noticeable in the case of $H_\alpha$ and least in the case of $H_\gamma$. Using a long tube of 2 cm. bore the ratio $I_k/I_l$, on changing the pressure from 0·1 mm. to 0·01 mm., increases by 50% for $H_\alpha$, 11% for $H_\beta$, and 5% for $H_\gamma$. The ratio $I_k/I_l$ is that of the intensity of the short wave-length component to the intensity of the long wave-length component. The change of the intensity relationship is nearly inversely proportional to the square of the series number. The bore of the tube has a controlling influence on the intensity relationship, thus, in a 5 cm. long tube of 1·5 mm. bore the longer wave-length component is stronger, but both components are faint. The appearance of the lines is unchanged on changing the bore from 5 mm. to 0·1 mm. J. F. S.

**Spectrum of Bromine Vapour; Zeeman Effect.** G. RIBAUD (*J. Phys.*, 1917, **7**, 205—208).—The emission spectrum of bromine

vapour was studied with the aid of a Geissler tube discharge. If a Geissler tube is placed perpendicularly to the field of an electromagnet, and strong fields are used, the apparent resistance of the tube becomes extremely high, and the discharge requires, therefore, a very high potential; moreover, the lines obtained are much broadened and difficult to measure. The tube is consequently introduced along the axis of the pole-pieces. Twenty-six lines in the region λ 4014 to λ 5332 were studied in a field of 21800 gauss. The values of $\Delta^{\lambda}/H\lambda^2$ for the majority of the lines are grouped about the values $1\cdot05\times10^{-4}$ and $1\cdot23\times10^{-4}$. Normal separation was not observed for any of the lines, but the lines λ 4766, 4785, and 4816 have a separation very nearly double the normal (cf. A., 1912, ii, 1114; Kimura, A., 1921, ii, 140, 141).

CHEMICAL ABSTRACTS.

**Excitation of the Enhanced Spectrum of Magnesium in a Low Voltage Arc.** PAUL D. FOOTE, W. F. MEGGERS, and F. L. MOHLER (*Phil. Mag.*, 1921, [vi], **42**, 1002—1015).—A vacuum arc is described in which the electronic–atomic collisions take place at any desired definite velocity of the electrons. The neutral magnesium atom is shown to absorb quanta of the following values, which may be emitted as equivalent quanta of radiation: 46·9 volts, producing *L*-radiation; 22·8 volts (probably), producing double ionisation and resulting in the simple enhanced and the arc spectra; 7·61 volts, producing simple ionisation and resulting in the arc spectrum; 2·70 volts resulting in the single line spectrum. The simply ionised magnesium atom absorbs quanta as follows: 14·97 volts, producing double ionisation and resulting in the simple enhanced spectrum; 4·4 volts resulting in the single-line enhanced spectrum. With high current density other quanta may be absorbed corresponding witb fundamental lines of the subordinate series.

J. F. S.

**Band Spectra of Isotopes.** L. GREBE and H. KONEN (*Physikal. Z.*, 1921, **22**, 546—549).—The wave-lengths of the higher members of the band spectrum of uranium-lead and ordinary lead have been compared. The chosen wave-lengths lie between λλ 4257·690 and 4281·458 Å.U. Eighteen lines have been compared, and it is shown that the wave-length of the line corresponding with uranium-lead is on the average 0·055 Å.U. shorter than that for ordinary lead. This figure agrees so far as its order is concerned with the assumption that the diatomic molecules are the carriers of the band spectrum.

J. F. S.

**Wave-lengths of Lines in the Iron Arc from Grating and Interferometer Measurements, λ 3370—6750.** CHARLES E. ST. JOHN and HAROLD D. BABCOCK (*Astrophys. J.*, 1921, **53**, 260—299).—One thousand and twenty-six lines were measured with an accuracy of ±0·001 Å. Manipulative details, receive special consideration in this paper.

CHEMICAL ABSTRACTS.

**Determination of the Terms of the Cyanogen Bands.** A. KRATZER (*Physikal. Z.*, 1921, **22**, 552—555).—A theoretical

paper in which the relationships of the violet cyanogen bands are investigated and the values obtained theoretically are compared with the experimental and empirical values of Heurlinger (*Z. Physik.*, 1920, i, 82). It is shown that the zero lines of the violet cyanogen bands are expressed by the formula $\nu = 25797{\cdot}83 + n_1(2143{\cdot}88 - n_1 \times 20{\cdot}25) - n_2(2055{\cdot}64 - n_2 \times 13{\cdot}25)$, in which $n_1$ and $n_2$ are the quantum numbers. A comparison of the zero values calculated by this equation with the empirically deduced values of Heurlinger shows in most cases an astonishingly good agreement between the two sets of wave-lengths. The whole of the line systems of the violet bands of cyanogen may be calculated by the theoretically deduced formula. $\nu = \nu_e + B_1^{n_1} + n_1\nu_1^{\circ}(1 - n_1u_1x_1) - n_2\nu_2^{\circ}(1 - n_2u_2x_2) \pm 2mB_1^{n_1} + m^2(B_1^{n_1} - B_2^{n_2})$, where $\nu_e + B_1^{\circ} = 25797{\cdot}83$; $\nu_e = 25795{\cdot}91$; $\nu_1^{\circ} = 2143{\cdot}88$; $\nu_1^{\circ}u_1x_1 = 20{\cdot}25$; $2B_1^{n_1} = 3{\cdot}841 - 0{\cdot}0044n_1$; $\nu_2^{\circ} = 2055{\cdot}64$; $\nu_2^{\circ}u_2x_2 = 13{\cdot}25$ and $2B_2^{n_2} = 3{\cdot}705 - 0{\cdot}035n_2$. It now becomes possible to differentiate between the red cyanogen bands and the so-called nitrogen bands, sincc, as was shown by Heurlinger, the red cyanogen bands and the violet cyanogen bands have a common end term. J. F. S.

**The Absorption Spectrum of Hydrogen Chloride.** WALTER F. COLBY and CHARLES F. MEYER (*Astrophys. J.*, 1921, **53**, 300—309).—The hydrogen chloride absorption band extending from 3·16 to 3·70$\mu$ was observed by the use of apparatus similar to that described by Imes (*Astrophys. J.*, 1919, **50**, 251—276). The compensation chamber was found to be superfluous. The absorption chambers, 16 to 60 cm. in length, could be heated to incipient redness. The experiments confirmed results of Paton showing that heating increases the number of observable lines but does not change the wave-length. The wave numbers for 28 lines were tabulated and an equation was derived to represent them. The law of spacing is not parabolic, as has been supposed, but a cubic term is found to be necessary. CHEMICAL ABSTRACTS.

**An Absorption Band Spectrum for Water in the Region of Wave-lengths of Several Decimetres.** RICHARD WEICHMANN (*Physikal. Z.*, 1921, **22**, 535—544).—The method of the parallel wire system is so modified that it may be used for the determination of the refractive indices of liquids and gives results with an error of only 0·5%. An exciter has been constructed by means of which a practically monochromatic radiation up to $\lambda = 12$ cm. and of a sufficient intensity can be produced. The resonance curve has a perfectly smooth course and a decrement which in general does not exceed 0·04. The width of the spectrum lines is therefore not much greater than $\Delta\lambda = 1$ mm. In the spectrum of water over the range $\lambda = 65$ cm. to $\lambda = 27$ cm., three bands of anomalous dispersion are found, which at the same time are three absorption bands. The width of the two outside bands is approximately $\Delta\lambda = 3$ cm. The middle band is sharper and has a width of 0·5 cm. These results indicate that it is probable that water possesses a true absorption spectrum in the region of long wave-lengths, which is

a continuation of the usual long wave-length absorption spectrum of water. J. F. S.

**Action of Electrical Fields on Absorption Lines (*D*-Lines of Sodium Vapour).** R. LADENBURG (*Physikal. Z.*, 1921, **22**, 549—552).—The effect of electric fields of 100,000 volt/cm. on the *D* lines of sodium has been investigated. The sodium light was produced in a quartz capillary filled with a mixture of neon and helium, and was examined in a Lummer-Gehrcke spectroscope. It is shown that no resolution of the absorption lines occurs, but that probably the *p* and *s* components are displaced unequally in the same sense. It is shown that two fundamentally different kinds of electrical action on spectrum lines must be differentiated, (1) the symmetrical, relatively strong Stark effect, which is proportional to the field strength, and (2) the unsymmetrical effect, which is proportional to the square of the field strength and occurs when the influenced electron together with the Coulomb's force act, and in comparison with which the external field is to be regarded as small. J. F. S.

**Effect of a Strong Electrical Field on the Absorption Lines of Sodium Vapour.** R. LADENBURG (*Naturwiss.*, 1921, **9**, 667; from *Chem. Zentr.*, 1921, iii, 993).—The Stark effect has only been observed with emission spectra of gases under the influence of canal rays. Using a strong electrical field (150,000—200,000 volts/cm.) and a Lummer-Gehrke interference spectrometer, a marked asymmetrical effect on the absorption lines of sodium vapour in the yellow was observed, and a displacement in the red of 0·02 Å. G. W. R.

**Width of the Absorption Bands of the Rare Earths.** KARL F. HERZFELD (*Physikal. Z.*, 1921, **22**, 544—546).—A mathematical paper, in which the width and the influence of temperature on the width of the absorption bands of the rare earths is considered. The width is shown to be due to a Stark effect, which is brought about by the penetration, due to the vibration, into the electric fields of the neighbouring ions. This view is in keeping with the dependence of the width on the temperature and leads to widths for the bands which are of the correct dimensions. It is shown that observations on the width of the bands at very low temperatures will furnish information on the existence of an energy zero point. The strength of the electric field in water is estimated as of the order $5 \times 10^7$ volts/cm. J. F. S.

**Spectroscopy of Uranium and some Rare Earths.** G. MEYER and GREULICH (*Physikal. Z.*, 1921, **22**, 583—585).—The minimum concentration of solutions of salts of uranium, cerium, lanthanum, didymium, and thorium which may be detected spectroscopically has been ascertained. The illumination was produced in three ways: (1) sparks from a transformer of 10,000 volts were passed from a platinum wire to a bundle of platinum wires moistened with the solution, (2) a syrupy mixture of the salt solution with

phosphoric acid was placed in the platinum electrodes of a Miethe extra current apparatus, and (3) hollow carbon arc carbons were filled with the residue obtained on evaporating the solution to dryness. The following gives the *minimum concentrations* ($c$) in mg./c.c. and the wave-lengths of the lines visible at this concentration: cerium, λλ 3940·89, 4166·75; $c$=0·01; lanthanum, λ 3949·22; $c$=0·006; didymium, Nd λ 4061·27, 4325·80; Pr λ 4206·81, 4429·41; $c$=0·01; thorium, λλ 4391·30, 4382·10; $c$=0·01; uranium, λλ 4090·28, 5919·61, $c$=5·0. It is thus seen that the *minimum concentration of uranium is approximately 500 times greater than that of the other metals.* Experiments were made to ascertain the influence of other salts on the amount of the elements in question which could be detected. The value of $G=\mathrm{U}/(\mathrm{U}+M)\times 100$ has been determined, in which U and $M$ represent the amounts of uranium and the other element. It is shown that the presence of cerium, lanthanum, didymium, and thorium has very little effect on the visibility of the uranium lines; in all cases the value of $G$ approximates to unity. In the case of fifteen other elements examined with uranium, it is shown that $G$ has a considerable value. It is also shown that a knowledge of the value of $G=\mathrm{U}/(\mathrm{U}+\mathrm{Fe})\times 100=7$ gives a means of estimating the amount of uranium in a solution of a uranium salt. The method consists in *adding an iron salt to the solution until the persistent uranium* lines just vanish. In the case of a solution of uranium sulphate containing 15·8 mg./c.c., there was found, using this method, 15·4 mg./c.c. The influence of the addition of salts of iron, nickel, chromium, manganese, potassium, sodium, calcium, cobalt, lithium, aluminium, magnesium, uranium, cerium, didymium, and thorium on *the persistence of the spectrum lines obtained from solutions* of cerium, lanthanum, didymium, and thorium salts was also investigated. The values $100\mathrm{Ce}/(\mathrm{Ce}+M)$; $100\mathrm{La}/(\mathrm{La}+M)$; $100\mathrm{Di}/(\mathrm{Di}+M)$, and $100\mathrm{Th}/(\mathrm{Th}+M)$ vary between 0·5 and 1·0 for all cases except those in which sodium to cerium, of the above list, have been added. It therefore follows that the rare earths are detectable in much smaller quantities in mixtures than is uranium. J. F. S.

**Absorption of Ultra-violet Light.** THOS. H. DURRANS (*Perf. Essent. Oil Rec.*, 1921, **12**, 370—371).—The ultra-violet absorption spectra of eugenol, *iso*eugenol, methyl*iso*eugenol, anethole, methylchavicole, and anisole were examined. *iso*Eugenol absorbs more strongly than eugenol, and methylation of the phenolic group still further increases the absorption, an *N*/10,000 solution being opaque in thicknesses greater than 20 cm. The absorptive power of anethole is remarkable, 10 cm. of *N*/10,000 solution or 0·25 mm. of pure anethole completely stopping ultra-violet light of a wave-length of less than about 27 Å.U. The substitution of the propenyl side-chain by the allyl radicle, or its complete removal, causes an enormous diminution of the absorptive power. The paper is illustrated by photographs of the absorption spectra of the substances examined. G. F. M.

**Absorption of Light by Solutions.** HARALD LUNELUND (*Öfvers. Finska Vet.-Soc.*, 1916—1917, 59, No. 21, 21 pp.; from *Chem. Zentr.*, 1921, iii, 810).—Working with aqueous solutions of "brilliant safranine," "tartrazine," "crystal-ponceau," and "rose Bengal" with and without addition of sulphuric acid, it was shown that the extinction coefficient, $\epsilon$, calculated from the formula $I' = I \cdot 10^{-\epsilon d}$, agrees with Beer's law, according to which the extinction coefficient is proportional to the concentration. Using the König-Martens spectral photometer, it is shown that in aqueous solutions of safranine a marked maximum absorption occurs for $\lambda$ 519$\mu\mu$. By addition of sulphuric acid the colour changes to green through violet, and the absorption maximum changes to $\lambda$ 622$\mu\mu$. G. W. R.

**A Theory of Chromo-isomerism of Solid Compounds.** HOWARD J. LUCAS and ARCHIE R. KEMP (*J. Amer. Chem. Soc.*, 1921, **43**, 1654—1665).—See this vol., i, 30.

**Hydrated Boric Acid as the Basis of Systems Capable of [Showing] a High Phosphorescence.** E. TIEDE, P. WULFF, and A. RAGOSS (*Physikal. Z.*, 1921, **22**, 563).—When boric acid is mixed with certain organic substances, particularly aromatic and heterocyclic substances, and partly dehydrated by melting, it is found on cooling that the mixtures are strongly phosphorescent. These substances after illumination by ultra-violet light emit a phosphorescent glow of a colour which varies with the organic substance and in the best cases persists for two to three minutes after the exciting light is removed. J. F. S.

**Destruction of Phosphorescent Zinc Sulphides by Ultra-violet Light.** LEONARD B. LOEB and LLOYD SCHMIEDESKAMP (*Proc. Nat. Acad. Sci.*, 1921, **7**, 202—207).—Three different samples of phosphorescent zinc sulphides were exposed in very thin layers to the action of ultra-violet light from a mercury arc. In each case there was a marked decrease in phosphorescent intensity (measured by a phosphoroscope) with increase of time of ultra-violet illumination. The reduction of intensity was accompanied in each case by a darkening in colour. Exposure to chlorine restored to some extent the original colour and ability to phosphoresce. Some points of similarity with the destruction of phosphorescence by the bombardment of $\alpha$-particles are discussed. G. W. R.

**Linear Polarisation of the Blue Light from the Focus of the Lilienfeld Röntgen Tube.** H. SEEMAN (*Physikal. Z.*, 1921, **22**, 581—582).—It has been shown by Lilienfeld and Rother (*ibid.*, 1920, **21**, 249, 360) that the light from the point of convergence of the Lilienfeld tube is almost completely linear polarised in the sense that the vibrations of the electric vector are at right angles to the plane of the anti-cathode which is inclined generally at 45° to the direction of the cathode rays. The present paper shows that this phenomenon can be observed without special apparatus

in full daylight by means of a Nicol prism held before the eye. The phenomenon is not observed in Coolidge or Müller electron tubes because of the very intense white light. J. F. S.

**Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. IV. Aryl Derivatives of Bisiminocamphor.** BAWA KARTAR SINGH, MAHAN SINGH, and JIWAN LAL (T., 1921, **119**, 1971—1976).

**Negative Optical Anomalies.** GERVAISE LE BAS (*Chem. News*, 1921, **123**, 271—272).—From a study of certain thiophen derivatives, it is shown that substitution $\alpha$ 2 in position 3 can reduce the negative anomaly of sulphur to zero. Substitution on both sides of the sulphur atom practically neutralises the negative anomaly. The full substitution of one ethenoid group or substitution on one side of the molecule reduces the negative anomaly to half its value. Chlorine and bromine have lost their usual positive anomalies for substitution in these cases. W. G.

**Mechanism of the Photochemical Chlorine-Hydrogen Gas Reaction and the Question of the Damping of the Velocity [of Reaction] of Chlorine Activated by Light.** RUDOLF GÖHRING (*Z. Elektrochem.*, 1921, **27**, 511—518).—The paper opens with an account of the principal investigations on the photochemical reactions between hydrogen and chlorine which have been carried out in the last twenty years. The possible reactions which may occur photochemically in a mixture of chlorine, hydrogen, and a little oxygen after the reaction $Cl_2+L=2Cl$ are considered. From a large number of possible combinations of reactions two sets are picked out, which both conform to Bodenstein's empirical reaction equation. The Bodenstein equations are theoretically deduced. The light absorption by chlorine has been measured for several wave-lengths and the fraction of light absorbed from the radiation of an Osram lamp has been calculated. It is shown that the number of quanta absorbed by 1 c.c. per sec. is approximately $2\times10^{11}$. The number of collisions calculated for the gas theory and the number of absorbed quanta are compared with reaction velocity calculated by Bodenstein. It is shown that for $1h\nu$ the number of molecules of hydrogen chloride formed is $5\times10^5$. Inserting the collision number and the measured reaction velocity in the equations deduced does not lead to any contradiction of the initial assumptions. The time required for damping of the activity of chlorine activated by light is calculated, and it is shown that theoretically no effect was to be expected in the experiments of Bodenstein and Taylor (A., 1916, ii, 463), although under other definite conditions an effect might have been observed. J. F. S.

**The Decomposition of Ozone by Light of the Visible Spectrum.** ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT (T., 1921, **119**, 1948—1959).

**Verification of the Photochemical Equivalent Law with Photographic Dry Plates.** J. EGGERT and W. NODDACK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 631—635).—Dry plates

of various kinds have been illuminated with light of wave-length 407·8$\mu\mu$ for measured periods of time and the amount of metallic silver formed by the absorption of a measured amount of light energy has been ascertained. It is shown that for a given type of dry plate (Agfa reproduction) the ratio $N/Q$, where $N$ is the number of silver atoms formed by an amount of light energy $Q$ quanta is constant and equal to 3·0%, that is, the production of one atom of silver requires 3% of the light energy striking the plate. The light absorption by the non-illuminated plate has been directly measured and is shown to be about 12—15%. A further experiment shows that about one hundred times as many quanta are absorbed as are silver nuclei formed. This indicates that about 100 quanta must act on a single particle before it can be reduced by the developer. The results point definitely to the conclusion that not every absorbed quantum produces a silver particle, but, in the case of moderate illumination, every silver particle corresponds with one and only one absorbed quantum. This is in keeping with the experimental result that the number of developed nuclei is proportional to the amount of absorbed light.

J. F. S.

**Photochemistry of Silver Compounds.** FRITZ WEIGERT and W. SCHÖLLER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 641—650).—Experiments have been carried out in silver chloride emulsions with the object of ascertaining the mechanism of the photographic copying process. It is shown that silver chloride is, of itself, neither light sensitive, nor does it furnish a noticeable quantity of the silver which constitutes the photographic positive. The colloidal metallic silver, which is present as an impurity in very small amounts in fresh unilluminated emulsions, is the only light sensitive substance present. The colouring of the emulsion layers therefore commences very slowly and after a while accelerates itself for a short time and then the rate of colouring decreases since the photographic yield in such solid systems is smaller with increasing quantities of silver. This behaviour is represented by an S-shaped curve which is obtained by plotting the amount of silver formed as ordinates against the time of illumination. The strong colouring in systems rich in silver acts in the same sense, since the silver behaves as a harmful light filter. The fact, that in this case the substance, which is light sensitive, is produced by the process itself, shows that the photochemical process takes place in molecules other than those which actually absorb the light. Since the system is solid the transmission of energy from the absorbing molecules to the reacting molecules cannot take place through collisions as in gaseous systems. It is therefore probable the energy transmission occurs by means of electrons. In a single atom, as, for example, the absorbing silver atom, no process other than the separation of an electron can occur through the absorption of an energy quantum. The electron is absorbed by the surrounding silver salts with the production of a photo-electric effect.

J. F. S.

**Action of Ultra-violet Light on Colloidal Platinum.** ELLWOOD B. SPEAR, P. F. JONES, A. S. NEAVE, and M. SHLAGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1385—1391).—A number of experiments on the coagulating action of ultra-violet light on platinum sols of various concentrations have been carried out at 20—22°. It is shown that ultra-violet light will precipitate colloidal platinum from solutions which contain no electrolytes other than carbon dioxide or constituents of the hard glass containers. Thus a solution containing 0·038 gram of platinum per litre was half coagulated in ten hours by ultra-violet light, whilst in the absence of ultra-violet light coagulation was not complete in two years. Coagulation by electrolytes is greatly accelerated by ultra-violet light. Thus a solution containing 0·038 gram of platinum was half coagulated in seven minutes by a solution of sodium chloride containing 4·25 millimols per litre when the action took place in ultra-violet light, but when no ultra-violet rays were employed sixty-four minutes were necessary to accomplish the same change. The action of ultra-violet light is greater in dilute solutions than in concentrated solutions of the colloids. J. F. S.

**The Action of Light of Short Wave-lengths on some Organic Acids and their Salts.** FRANS MAURITS JAEGER (T., 1921, **119**, 2070—2076).

**Photochemistry of the Retina.** FRITZ WEIGERT (*Z. Elektrochem.*, 1921, **27**, 481—487).—The processes occurring in the retina are considered and an hypothesis of the action is advanced on the basis of experiments on the velocity of bleaching of layers of collodion containing dyes by polarised light. The velocity of bleaching of layers of collodion containing cyanine by linear polarised light has been examined spectro-photometrically and dichrometrically. It is shown that the velocity of bleaching of a freshly-prepared layer is much greater than that of an already partly bleached layer of the same extinction. It is also shown that layers of dyes resemble very strongly the photochlorides. J. F. S.

**Phototropy and Photoelectric Effect.** PATRICK H. GALLAGHER (*Bull. Soc. chim.*, 1921, [iv], **29**, 961—976; cf. A., 1921, i, 715). —The author has applied the method of Padoa and Amaduzzi (cf. A., 1912, ii, 227) in a modified form to a study of photo-electric effects in relationship to phototropy in the case of a number of aldehyde-amines. Phototropic compounds show photo-electric fatigue on exposure to the light from a mercury lamp much more slowly than other substances. The results seem to indicate that in phototropic transformations there is a liberation of electrons. An electron so liberated will take up a new position in the molecule or will remain at some distance from the molecule in a state of forced equilibrium. Its intervention in the photo-electric effect will be secondary. The relationship between phototropy and phosphorescence and fluorescence is considered. W. G.

**Passage of α-Rays through Materials.** H. Rausch von Traubenberg and K. Philipp (*Physikal. Z.*, 1921, **22**, 587—588).—The range of α-rays in liquids and gases has been investigated. The range of the α-ray in water is found to be 60μ. In the case of gases, carbon monoxide, carbon dioxide, methyl bromide, methyl iodide, chlorine, hydrogen chloride, and ammonia have been investigated and results obtained which agree with the results obtained by Bragg by the ionisation method. In the case of liquids, the range was measured by immersing a Sidot screen in the liquid until it just fluoresced and measuring the thickness of the liquid layer with a horizontal microscope. The range in gases was obtained by passing the beam of rays parallel to the horizontal side of a glass wedge containing the gas and placing in the path of the rays a Sidot screen at a small angle to the horizontal. By observing the boundary of dark and light on the screen, the range may be deduced. Taking oxygen as standard, it is shown that the stopping power of the gases varies as $\sqrt{Z}$. It is shown that the stopping power of compounds is not strictly additive as Bragg has stated, and it is now shown that the stopping power of hydrogen varies in different compounds, thus $H_2$, 0·200 per atom; but in the compounds $C_2H_2$, $C_2H_4$, $C_2H_6$, $CH_4$, 0·187; $NH_3$, 0·173; and HCl, 0·16.
J. F. S.

**Collisions of α-Particles with Hydrogen Nuclei.** J. Chadwick and E. S. Bieler (*Phil. Mag.*, 1921, [vi], **42**, 923—940).—The relationships which hold in the collisions between α-particles and hydrogen nuclei have been investigated. The angular distribution of the hydrogen particles projected by α-particles of mean range 6·6 cm. has been determined up to an angle of 66°. The distribution for α-rays of mean ranges 8·2, 4·3, and 2·9 cm. has been obtained over a smaller range of angle. It is shown that the number of hydrogen particles projected within these angles by α-rays of high velocity is greatly in excess of that given by forces varying as the inverse square of the distance between the centres of the two nuclei. The variation in the number of hydrogen particles projected within a given angle with the velocity of α-rays has been observed over a wide range. It is shown that for α-rays of high velocity the variation is in the opposite direction to that given by the inverse square law; for α-rays of range less than 2 cm. and velocity less than $1·26\times10^9$ cm. per sec., however, the collision relation is about the same as that given by the inverse square law. The experimental collision relation is compared with those calculated by Darwin for various models of the α-particle, and the conclusion is drawn that the α-particle behaves in these collisions as an elastic oblate spheroid of semi-axes about $8\times10^{-13}$ and $4\times10^{-13}$ cm., moving in the direction of its minor axis. Outside this surface, the force varies approximately as the inverse square of the distance from the centre of the spheroid. J. F. S.

**Recoil of Hydrogen Nuclei from Swift α-Particles.** A. L. McAulay (*Phil. Mag.*, 1921, [vi], **42**, 892—904).—An account of

work undertaken to ascertain the number of atoms recoiling at various angles from an homogeneous α-ray beam, from thorium-*C* and radium-*C* respectively with the object of obtaining data bearing on the nature of the collisions, the size of the colliding particles, and similar quantities. The experimental method was similar in principle to that already described (*ibid.*, 1920). An experiment made to determine the relation between the α- and γ-ray activity of thorium-*C* is described. J. F. S.

**The Oxidising Properties of certain Radioactive Elements.** PIERRE LEMAY and LÉON JALOUSTRE (*Compt. rend.*, 1921, **173**, 916—918).—The bromides of mesothorium, radiothorium, thorium-*X*, and radium were found to be catalysts of certain oxidation reactions. Their action is not due to the intermediate formation of ozone but to α-radiation, and, for the small amounts of material used, it is the same for the four elements. W. G.

**Scattering of β-Rays by Thin Metal Sheets.** H. GEIGER and W. BOTHE (*Physikal. Z.*, 1921, **22**, 585—587).—The scattering of β-rays by thin metal sheets has been measured (*a*) in the region of small scattering angle ($\phi=15°$ or less) and (*b*) in regions of large scattering angle ($\phi=60°$ or more). It is shown that there is a fundamental difference between the two types of scattering. In the region of smaller angles, the observed angle is produced by the superposition of many individual small scattering angles through which the β-ray is bent as it passes the individual atoms (multiple scattering), whilst in the region of larger angles the superposition plays a subordinate rôle; each scattering angle is produced by a single collision of a β-ray with a single atom. This is relatively rare, for it is only brought about when the path of the electron lies very close to the nucleus of the atom (individual scattering). In the case of β-rays from radium-($B+C$), it is shown that for the very thinnest layers (under 0·01 mm.) the scattering is less than that demanded by the square root law, but for thicker layers this law is confirmed. There is an inverse proportionality between $mv^2$ and the probable scattering angle, if the uncertain measurements for β-rays of high velocity are left out of account.

J. F. S.

**Excitation of γ-Radiation by α-Particles from Radium Emanation.** F. P. SLATER (*Phil. Mag.*, 1921, [vi], **42**, 904—923).—A hard γ-radiation is emitted when α-particles from radium emanation impinge on metals such as lead and tin. The radiation differs but little in quality when the radiator is changed from one of high atomic number to one of low atomic number. The coefficients of absorption in lead are 1·8 cm.$^{-1}$ for lead and 2·1 cm.$^{-1}$ for tin. The intensity obtained is very small, and only a small fraction of the impinging α-particles can be effective. For the same absorption conditions the intensity is about 50% greater for the lead radiation than for the tin radiation. It appears to be emitted fairly uniformly in all directions, but differs in all other respects from the characteristic radiations, and is probably emitted from

the nuclei of the atoms in the radiator after direct collision with the α-particles. No hard radiation is emitted by the disintegration of the radium emanation nucleus in the ordinary course of radioactive transformation. Elements of high atomic number when bombarded by α-particles emit two well-defined types of radiation, corresponding roughly with their characteristic $K$ and $L$ radiations. Tin, an element of medium atomic number, emits one type, within the range of the experiments, of quality roughly the same as its $L$ radiation. The quantity of radiation emitted by any element is so small that a very small fraction of the impinging α-particles can cause radiation. Radium emanation emits, under the conditions of the experiments, no soft radiation on disintegration.

J. F. S.

**Excitation of Soft Characteristic X-Rays.** O. W. RICHARDSON and C. B. BAZZONI (*Phil. Mag.*, 1921, [vi], **42**, 1015—1019).—A development of work previously published by the authors (A., 1917, ii, 521). The thermionic radiation from a tungsten wire has been allowed to fall on targets of carbon, molybdenum, copper, and tungsten and in all cases an emission of radiation has been detected. In the case of carbon and molybdenum, the critical potential at which radiation sets in has been determined with considerable exactitude. In the case of carbon, the target was prepared on a copper disk from india-ink, and the thermionic current was kept constant by reducing the temperature of the filament as the operating voltage was increased. Although the pressure was of the order $10^{-8}$—$10^{-9}$ mm., a radiation effect was present at 220 volts which may have been due to residual gas as it was independent of the voltage above 220 volts. A radiation occurs at 286 volts. If it be admitted that the radiations are soft $X$-rays excited according to the same laws as hard $X$-rays and the quantum relation is applied, it is found that the wave-length of the shortest member of the group lies between 42·7 and 44·3 Å.U. and is probably close to 43·4 Å.U. Extrapolating from $K_\beta$ for aluminium and using Moseley's relation, it is found that $K_\beta$ for carbon should have the wave-length 45·5 Å.U. This makes it practically certain that the radiation is the $K$ series of carbon. In the case of molybdenum, radiation is obtained at 356 volts, which corresponds with the wave-length 34·8 Å.U. Calculating from Vegard's empirical relation, the $M_\alpha$ line of molybdenum should be 35·2 Å.U., which indicates that the radiation is the $M$ series of molybdenum.

J. F. S.

**Scattering of Röntgen Rays by Anisotropic Liquids.** E. HÜCKEL (*Physikal. Z.*, 1921, **22**, 561—563).—The scattering of Röntgen rays by *p*-azoxyanisole, *p*-azoxyphenetole, dianisylideneazine, cholesteryl propionate and cholesteryl benzoate as solid, clear-liquid, and turbid-liquid crystals has been photographed with the object of ascertaining whether or no the liquid crystals possess a space lattice. Several of the photographs are reproduced in the paper, and show that the turbid liquids do not consist of

regions built up on a space lattice, and, further, that in the suspended liquids there is no noticeable amount of material built up on a space lattice. It is not impossible, however, that small quantities of crystals are suspended in the liquid, since the interference bands which they would produce are too weak to be visible. It is shown that the term anisotropic liquids must be used in place of that of liquid crystals, for the word crystal implies a space lattice. If this is not adopted it will be logical to term as crystals a gas with molecules which carry electric dipoles in an electric field, also paramagnetic gases in a magnetic field. Consequently, it is to be taken that anisotropic liquids possess a more or less ordered arrangement of their molecules on account of their electrical and magnetic characteristics. J. F. S.

**A Precision Röntgen Spectrograph.** H. SEEMANN (*Physikal. Z.*, 1921, **22**, 580—581).—A Röntgen spectrograph is described which is designed to measure lines of the hardest spectrum region. Using rock salt, reflecting crystal measurements may be made beyond 1 Å.U., and also in the softest technical Röntgen spectrum by using a gypsum reflecting crystal, measurements may be obtained beyond 3 Å.U. The instrument is designed for both the camera and window methods of measurement. J. F. S.

**Fine Structure of Röntgen Spectra.** ADOLF SMEKAL (*Physikal. Z.*, 1921, **22**, 559—561).—A theoretical discussion of the fine structure of Röntgen spectra in which it is shown that if the sum of the quanta of an electron layer is $k$, that is, the layer is $k$-quantal, then the number of energy levels belonging to the layer is $2k-1$. According to Bohr, the $O$-layer of the heaviest elements is tri-quantal and the $P$-layer is di-quantal; it follows that there must be $5O$ and $3P$ energy levels. Wentzel has shown by means of his principle of selection that the $O$-layer is actually tri-quantal. J. F. S.

**The Existence of a New Radioactive Emanation in the Springs of Bagnoles-de-l'Orne and its Surroundings.** P. LOISEL (*Compt. rend.*, 1921, **173**, 1098—1101).—In studying the gases dissolved in the water of a large number of springs in the region of Bagnoles-de-l'Orne, a curve of activity was obtained which could not be explained by the presence of any known emanation. The curve showed at first a decreasing activity, then a rise to a maximum, followed by a decrease. The results indicate the presence of a new, simple, radioactive substance, to which the author provisionally gives the name *emilium*. W. G.

**Radioactivity and Atomic Constitution.** LISE MEITNER (*Naturwiss.*, 1921, **9**, 423—427; from *Chem. Zentr.*, 1921, iii, 847).—A discussion of the subject of isotopes in relation to atomic transformations. From a formula connecting the number of nuclear constituents with the number of helium nuclei and the number of electrons, four possible types of atomic disintegration of radioactive elements are deduced. G. W. R.

**Adsorption of Radium by Barium Sulphate.** FRANK E. E. GERMANN (*J. Amer. Chem. Soc.*, 1921, **43**, 1615—1621).—From experiments on the adsorption of radium, from a radium barium chloride solution, containing $22{\cdot}79\times10^{-10}$ gram of radium per c.c., by barium sulphate, it is shown that Kroeker's adsorption law is true in the case of the adsorption of a radioactive substance. The adsorption law of Freundlich is found to be equally true in the case of a radioactive substance. Consequently, it follows that the laws which apply to the adsorption of easily weighable masses also apply with an equal degree of accuracy to masses of the order $5\times10^{-8}$ gram adsorbed by 1 gram of adsorbent. The relationship existing between adsorption taking place during precipitation and that taking place on a solid precipitate of definite surface area has been discussed. J. F. S.

**The Radioactivity of Mineral Springs. II.** ERICH EBLER and A. J. VAN RHYN (*Z. anorg. Chem.*, 1921, **119**, 135—144; cf. A., 1911, ii, 1049).—Borings for thermal water undertaken by the town of Heidelberg in 1913 provided an opportunity for studying the relationship of radium to radium emanation content and the influence of depth and geological considerations on the radioactivity of the water. The waters from these borings were also compared with those from other springs. In the Heidelberg waters the radium emanation content was constant at about $10^{-10}$ "Curie" per litre, and was independent of the depth of the boring down to 600 m. The granite springs of Löwenbrunnen show a higher and the New Red Sandstone springs of Felsenmeer a lower emanation content, in agreement with the known relatively high radium content of granite and the low radium content of sandstones. The radium salt content of the water from the Heidelberg borings was of the order $10^{-12}$ gram per litre, but rose at a depth of 590 m. to $0{\cdot}97\cdot10^{-10}$, of the same order as that in the Max spring at Bad-Dürkheim (*loc. cit.*). This observation supports the view that the radium content increases with the depth of the spring. The granitic water of Löwenbrunnen does not show a high radium salt content corresponding with its high emanation content. It is important when comparing different waters to measure both radium and radium emanation content, as these may vary independently of each other. E. H. R.

**The Adsorption of Radioactive Substances. II.** ERICH EBLER and A. J. VAN RHYN (*Ber.*, 1921, **54**, [*B*], 2896—2912; cf. A., 1911, ii, 957).—The view has been expressed previously (*loc. cit.*) that the colloidal condition does not exercise a directive influence on the behaviour of colloids towards radio-elements, but that this depends on the chemical nature of the substances, the reactions which occur being expedited by the increased surface. Thus, the adsorption of radioactive material by silica or, more precisely, by its hydrate, is due to the formation of sparingly soluble silicates which owe their origin to the acidic nature of the hydrate. The discordant results obtained by many observers

are due to the fact that the acidity of the solution plays an important part, since acid has a de-adsorbent action probably in accordance with the scheme: $RaSiO_3+2HCl=RaCl_2+H_2SiO_3$. In addition, the silicic acid and its gels which have been used are very ill-defined products which, owing to the number of factors affecting their condition, are frequently not reproducible. In this connexion it is pointed out that the statement of Horovitz and Paneth (A., 1915, ii, 305) that the separation of silica during the estimation of radium in minerals is of no importance is only true within certain limits, since if free acid is not present in considerable quantity, the precipitate carries down radium.

The adsorptive power of charcoal for radioactive material appears difficult to explain in the light of the hypothesis outlined above. It is pointed out, however, that the varieties of charcoal employed never consist of pure carbon. In a series of experiments the adsorptive power of blood and animal charcoal towards uranium-*X* has been compared with that of pure charcoal in differing degrees of fineness (prepared by the carbonisation of pure sugar, extraction of the residue with water, and ignition of the product at bright redness). It is found that the selective adsorption of uranium-*X* by pure carbon is very much less than that of the impure varieties. An active preparation is obtained, however, when pure charcoal is mixed with the residues prepared by extracting blood or animal charcoal with water or dilute acid and subsequent evaporation of the extracts to dryness. The adsorptive power of impure charcoal, therefore, appears to be due to the impurities contained in it.

The adsorption of radium by barium sulphate has been examined further. This so-called "precipitation" of radium sulphate is not, in reality, a precipitation in the usual sense since, on account of the small concentration of radium, the solubility product $L=K.C_{Ra}.C_{SO_4}$ is seldom attained. It is shown that co-precipitation of radium sulphate with barium sulphate from solutions containing radium and barium is only complete when the barium is completely precipitated. An exact distribution of radium between the solid and liquid phase does not appear to occur.

H. W.

**The Adsorption of Thorium-*B* and Thorium-*C* by Ferric Hydroxide.** JOHN ARNOLD CRANSTON and ROBERT ALEXANDER BURNETT (T., 1921, **119**, 2036—2044).

**Excitation of Atoms to Emission of Light by Electronic Collisions. IV. Behaviour of Individual Members of a Series.** R. SEELIGER (*Physikal. Z.*, 1921, **22**, 610—613; cf. A., 1921, ii, 143, *Z. Physik.*, 1920, i, 355; 1921, **5**, 182, **7**, 93).—An examination of the spectra of helium, hydrogen, mercury, and neon produced by collisions with electrons shows that two kinds of series are produced, the one, which shows the regular behaviour, namely, that the optimal velocity increases with increasing member number, and the intensity maximum is displaced toward

the cathode with increasing member number, and the other, where the opposite behaviour is observed. To the first belong the Balmer series of hydrogen and both subsidiary triplet series of mercury, whilst to the second belong, the series of neon and helium.

J. F. S.

**Entropy of Electron Gas.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1592—1601).—It is shown that considerable simplification in expression and thought can be achieved by treating electrons as atoms of a chemical substance. This substance, which may be regarded as a gas "*plus que parfait*," owing to the very considerable force of repulsion between electrons, will not deviate appreciably in behaviour from a perfect monatomic gas if the concentration is low enough and the temperature high enough so that the effects produced by the repulsive force between the electrons can be neglected in comparison with the effect produced by their thermal agitation. It is shown with a reasonable certainty that the entropy of electron gas may be calculated from the theoretical equation, $S=5/2R \log_e T-R \log_e p+3/2R \log_e M+S_1$, which is found to apply to the monatomic gases. Using this equation, the entropies of 1 mol. of electron gas in equilibrium with metal filaments at 2000° are found to be: tungsten 53·3, tantalum 52·3, molybdenum 51·0. The entropy may also be calculated from the heat of vaporisation of the electron gas by the equation $S=\Delta H/T$, in which $\Delta H$ is the heat absorbed when 1 mol. of electrons is reversibly evaporated at $T$. The following values are obtained: tungsten, $\Delta H=107270$ cal., $S=53{\cdot}6$; tantalum, $\Delta H=107970$ cal., $S=54{\cdot}0$; molybdenum, $\Delta H=109770$, $S=54{\cdot}9$.

J. F. S.

**Thermal Ionisation of Metallic Vapours.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1630—1632).—Making use of work recently published on the entropy of electron gas (see preceding abstract) it is shown that further information on the thermal ionisation of metallic vapours may be obtained. Thus assuming that a metallic vapour can ionise into a positive ion and an electron thus: $R=R^{+}+E^{-}$, it is shown that $\Delta F=EQ-5/2RT \log_e T+(5/2R-3/2R \log_e M_E-S_1)T$ which connects the free energy with the heat content and the entropy and is of the same form as the well known free energy equation $\Delta F=\Delta H_0-\Delta C_pT \log_e T+IT$. The ionisation constant is given by the equation $\log_e K_p=-EQ/RT+5/2 \log_e T-(5/2-3/2 \log_e M_E-S_1/R)$, or, putting in the numerical values of the constants $Q=96540$ coulombs, $M_E$ (the molecular weight of electron gas) $=5{\cdot}44\times10^{-4}$ gram. $S=-3{\cdot}2$ cal./degree and $R=1{\cdot}985$ cal./degree the equation becomes: $\log_e K_p=-5040E/T+2{\cdot}5 \log T-6{\cdot}69$, where $E$ is the ionisation potential in volts. Using the above formulæ, the author calculates the ionisation of calcium in the sun. Taking the ionisation potential as 6·1 volts, the partial pressure of un-ionised calcium vapour as 4 atms., and the temperature as 5500° abs., it is found that the partial pressure of the calcium ion or electron gas is 0·07 atm., corresponding with 1·7% ionisation. J. F. S.

**New Detectors of High Frequency Vibrations.** W. Heike (*Z. anorg. Chem.*, 1921, **118**, 255—263).—An account of experiments made with the object of discovering an artificial detector for use as a substitute for pyrites in wireless telegraphy. Preparations of zinc arsenide, $ZnAs_2$, containing crystals of zinc antimonide, ZnSb, proved specially sensitive. The zinc–arsenic alloys are discussed in the succeeding paper (this vol., ii, 60).

E. H. R.

**Conductivity of Solutions of Ternary Electrolytes in Propyl Alcohol.** Charles A. Kraus and John Egbert Bishop (*J. Amer. Chem. Soc.*, 1921, **43**, 1568—1575).—The electrical conductivity of anhydrous calcium nitrate and magnesium nitrate hexahydrate in anhydrous propyl alcohol and magnesium nitrate hexahydrate in mixtures of propyl alcohol and water has been determined at 18° for a series of concentrations. The present results are compared with those of Schlamp (A., 1894, ii, 376) on lithium and calcium chlorides and it is shown that his results indicate that the calcium chloride must have been hydrated. Neither the present work nor that of Schlamp supports the view that ternary salts ionise in this solvent according to a binary process. The specific conductivity of anhydrous propyl alcohol at 18° is $1{\cdot}7\times10^{-7}$. J. F. S.

**The Theory of Electrolytic Ions. XXVI. How is the Limiting Value of the Molecular Conductivity of Strong Electrolytes Determined?** Richard Lorenz (*Z. anorg. Chem.*, 1921, **118**, 209—222; cf. A., 1921, ii, 158, 481, 482, 483).—A graphic method for determining the limiting molecular conductivity $\mu_0$ of univalent electrolytes is described, based on Herz's theory of ionic conductivity (A., 1921, ii, 482). According to this theory, the conductivity of a single ion is expressed by the equation $B(\lambda_0-\lambda)=\psi(\omega)$, where $B$ is a constant and $\omega=A[S]^{\frac{1}{3}}$, where $A$ is another constant and $S$ is the concentration. The ionic conductivity $\lambda$ of the theory is identical with the molecular conductivity, $\mu$. The graphic method described depends on the fact that, by means of the constants $A$ and $B$, the $[S]^{\frac{1}{3}}$—conductivity curve of any substance can be transformed to coincide with a "universal conductivity curve." The molecular conductivities as ordinates are plotted against $[S]^{\frac{1}{3}}$ as abscissæ on a prescribed scale, and by a simple geometric process the curve obtained is transformed into a form of the universal curve. By comparing this derived curve with a series of standard curves printed on transparent paper on the same scale, the values of $\mu_0$ and of the constant $B$ can be read off on the ordinate axis. E. H. R.

**Concentration and Potential Fall at Boundary Surfaces.** H. Freundlich (*Z. Elektrochem.*, 1921, **27**, 505—511).—A theoretical paper in which the change in concentration and the *E.M.F.* at the boundary surfaces of two liquids is considered. It is shown that the concentration of saponin or amyl alcohol in the foam produced at the air–water interface is due to the lowering of the

surface energy at the interface. All cases of adsorption are shown to be fundamentally due to the same cause. The case of adsorption on crystal faces is particularly considered, and although in this case the adsorption is held to be due to residual affinity, it is shown that here the phenomenon is molecular-kinetic, whilst with the surface tension a thermodynamic function is employed. In the case of surface tension, the mean value of a large number of molecules is considered, whilst with crystal surfaces when considering the residual valencies individual molecules only are concerned. The *E.M.F.* existing at interfaces and the changes effected by the introduction of foreign non-electrolytes is considered.

J. F. S.

**The Normal Potential of Silver.** I. M. KOLTHOFF (*Z. anorg. Chem.*, 1921, **119**, 202—212).—The electrolytic potential of silver was measured in silver nitrate solutions varying in strength from 0·001 to 0·1*N* at 18° against a normal calomel electrode. The mean value found for the silver potential was −0·7887 volt against the normal hydrogen electrode. Potassium nitrate, up to a concentration of 1·0*N*, has no measurable effect on the potential of the silver electrode. From measurements with a silver–silver bromide electrode in solutions of potassium bromide from 0·001 to 0·5*N*, the solubility product of silver bromide at 18° was found to be $4·1 \times 10^{-13}$. The concentration of bromine ions can be calculated from the equation $\log[Br] = (-\pi - 0·34852)/0·0576$. In presence of sulphates in solution, the silver electrode becomes "nobler"; the same is true of the mercury electrode. E. H. R.

**Some Phenomena in the Electromotive Behaviour of certain Metals.** NIL RATAN DHAR (*Z. anorg. Chem.*, 1921, **118**, 75—80).—If the potential difference between a metal and a solution of one of its salts increases with increasing dilution, it is to be expected, by extrapolation of Nernst's formula, that the potential difference would be still greater when the metal is in contact with water or a solution of a neutral electrolyte. Conversely, if the *E.M.F.* decreases as the dilution increases, it should be still less in water or a solution of a neutral electrolyte. A large number of measurements were made to test these theoretical deductions. The metals magnesium, zinc, and aluminium gave each a smaller *E.M.F.* in water or a neutral electrolyte than in a solution of its own salt, instead of greater, as was to be expected. Similarly, nickel and tin, by giving greater *E.M.F.* in water or neutral electrolytes, behaved in a manner contrary to what was expected. Only the metals antimony, copper, and silver, which have small solution tensions, behaved in the way indicated by theoretical considerations. A large number of measurements were made of the *E.M.F.* given by pairs of the above metals in water and potassium chloride solution respectively. E. H. R.

**Electromotive Behaviour of Aluminium.** A. SMITS (*Z. Elektrochem.*, 1921, **27**, 523—526).—Polemical. An answer to the criticism of Gunther-Schulze (A., 1921, ii, 535) to the author's

paper (A., 1920, ii, 579) in connexion with anodic polarisation and passivity. The author maintains his former position. J. F. S.

**Electromotive Behaviour of Aluminium. III.** A. SMITS and C. J. DE GRUYTER (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 86—91; cf. A., 1920, ii, 579; 1921, ii, 371).—A continuation of previous work (*loc. cit.*). The influence of mercury on the potential of aluminium immersed in a solution of aluminium sulphate has been investigated. The aluminium electrode was placed in a solution of aluminium sulphate and small quantities of a mercury salt were added at intervals, and the potential was measured repeatedly. The influence of oxygen on the process was prevented by a stream of nitrogen which was continuously bubbled through the solution. It was found that the potential of the aluminium at first became less negative, reached a minimum, after which it rose to a strongly negative value which increased to a maximum. The maximum value was maintained for some time and then fell to a value which was close to the mercury potential. Up to the point where the maximum was observed, the aluminium electrode was grey in colour, but during the last stage it became lustrous, due to a coherent film of mercury. The changes are considered in connexion with the three-phase equilibrium of the four component system $Al^{\cdot\cdot\cdot}$—$Hg^{\cdot\cdot}$—anion—$H_2O$. J. F. S.

**Electrochemical Investigations of Gold–Copper Mixed Crystals.** RICHARD LORENZ, W. FRAENKEL, and M. WORMSER (*Z. anorg. Chem.*, 1921, **118**, 231—253).—In connexion with the study of discharge and decomposition potentials, experiments were made in which a series of gold–copper alloys were used as anodes in an electrolytic cell. For studying the discharge potentials, *N*/10-sodium hydroxide was used as electrolyte, with a copper cathode, and the cell was charged for a short time, about two minutes, with an *E.M.F.* of about 4 volts. The discharge potential was then plotted against time. With pure copper and with alloys containing less than 0·2 atom of gold, a distinct arrest occurred *in the curve, whilst alloys with 0·2 atoms of gold and upwards* behaved like pure gold, giving a smooth discharge curve. The charging, or decomposition, potentials were studied, using as electrolytes first a solution containing sodium hydroxide and ammonia, and then copper sulphate. In the former case, copper or an alloy with 0·1 atom of gold showed an early rise of current with *E.M.F.*, followed by a fall to zero and then a steady rise starting at about 0·7 volt. With 0·2 atom or more of gold, no current passed until the *E.M.F.* reached 1·05 volts, and the current increased steadily with the *E.M.F.* Using copper sulphate as electrolyte, the decomposition potential rose steadily with the gold content of the alloy up to about 0·25 atom of gold, and from 0·35 atom of gold upwards was indistinguishable from that of pure gold. This is in agreement with Tammann's observations on the limiting composition in gold–copper alloys (A., 1920, ii, 672). It is shown experimentally that

changes in the resistance of the cell during the experiments have no appreciable influence on the results obtained, and it follows that the maximum and minimum in the decomposition potential curves and the arrest point in the discharge potential curves for copper and the alloys less rich in gold have a common cause.

E. H. R.

**Metallographic Investigations on the Cathodic Deposition of Metals on Aluminium and Chromium.** S. KYROPOULOS (*Z. anorg. Chem.*, 1921, **119**, 299—304).—The cathodic deposition of copper, silver, chromium, and nickel on aluminium and chromium was studied. Copper and silver from nitrate solution, with a current density of 0·01 to 0·1 amp. per sq. cm., are deposited on tempered aluminium principally on the intercrystalline boundaries and to a very limited extent on the crystal faces, whilst chromium and nickel are deposited more freely in isolated spots on the crystal faces. With chromium and nickel, a higher current intensity favours deposition on the crystal faces of the aluminium. From cyanide solution copper may be deposited on the crystal faces when the current intensity is high; on pressed aluminium it is deposited along the gliding lines. It is noteworthy that deposition on the crystal faces is favoured under conditions such that production of hydrogen at the cathode is possible. Resistance to copper deposition is most clearly shown by passive chromium, deposition occurring only on isolated spots of non-passive metal or impurity. Under conditions which destroy the passivity of the chromium, such as hydrogen evolution at the cathode, deposition occurs on the crystal faces of the chromium. E. H. R.

**Electrolysis of Aqueous Solution of Cerous Salts.** A. B. SCHIØTZ (*Z. Elektrochem.*, 1921, **27**, 521—523; cf. A., 1921, ii, 589).—After a short account of the work which has previously been carried out on the electrolysis of solutions of the rare earth salts, and of that on the cerium alloys, experiments are described on the electrolysis of concentrated solutions of mixtures of cerous and ferrous chlorides to which various additions had been made. The electrolysis took place between a platinum spiral which served as anode and a platinum gauze covered with lead dioxide which served as cathode. The solutions, which were used warm, contained 30 grams of lactic acid neutralised by sodium or potassium hydroxide, and 5—10 grams of sodium chloride in 400 c.c. of water to which was added cerous chloride (7·0—3·5 grams) and ferrous chloride (4·5 grams). The electrolysis was effected with a current density of 0·4—2·0 amp./sq. cm. and yielded in all cases a black, powdery deposit which was metallic and contained about 62% of cerium. Whether or no it contained oxygen could not be ascertained because of the difficulty of drying the substance without oxidation. The deposit corresponds with the iron–cerium alloy, $Ce_2Fe_3$, prepared by Vogel (A., 1912, ii, 557). The electrolysis of cerous chloride in the presence of chloride of mercury, nickel, platinum, zinc, or aluminium gave deposits which contained no

cerium. The addition of potassium lactate to solutions of cerous chloride raises the overvoltage by 0·15 volt. J. F. S.

**Biochemical and Electrochemical Oxidation of Organic Compounds.** FR. FICHTER (*Z. Elektrochem.*, 1921, **27**, 487—494).—A general discussion of electrolytic and biochemical oxidation of organic substances in which a number of similarities in the two processes are indicated. J. F. S.

**Magnetism and the Constitution of Atoms.** PIERRE WEISS (*Rev. sci.*, 1920, **58**, 645—659).—A review of work already published (see A., 1911, ii, 91, 183, 250, 367, 694; 1915, ii, 737).
CHEMICAL ABSTRACTS.

**Behaviour of Substances near the Absolute Zero.** WILLIAM R. FIELDING (*Chem. News*, 1921, **123**, 97—99).—The results previously obtained by the author (A., 1920, ii, 732; 1921, ii, 487) are applied in the present paper to several substances in the neighbourhood of the absolute zero. Making use of the specific heat of lead determined by Kammerlingh Onnes and Keesom over the range 46°Abs.—14°Abs., the author has determined the specific heat over the range 14°Abs.—0°Abs. by three methods and finds that by plotting the specific heat curve the specific heat appears to be zero at 6°Abs., by plotting the specific heats against the absolute temperatures the values 10°Abs., $s=0·0053$, 2°Abs., $s=0·0012$ and 1°Abs., $s=0·00005$ are obtained, whilst applying Debye's law (atomic heat$=kT^3$) leads to values which demand that the molecule of lead must change from $Pb_8$ to $Pb_{(3000-4000)}$. Similar calculations are made for water, copper, and carbon, and the absolute molecular weight is calculated for the absolute zero. The values recorded are, water 540, lead 1456, and copper 9450. If the values of $p$, the number of single molecules in the complex molecule, are plotted, it becomes possible to obtain by extrapolation the values for other elements. The values of $p$ are shown to be periodic, thus, iodine 6·3, bromine 6·6, chlorine 14, and fluorine 24 all at 0°Abs. In the case of mercury, $p$ is slightly greater than 2. The number of atoms in the benzene, naphthalene, and anthracene polymerides at the absolute zero are respectively 84, 100, and 132. J. F. S.

**The Properties of Organic Liquids.** W. HERZ (*Z. anorg. Chem.*, 1920, **118**, 202—206).—The relation $T_c/d_c\sqrt{n}=$const., where $n$ is the number of atoms in the molecule, has been found to hold for 27 non-associated organic liquids and to have a value approximately equal to 450. When this is combined with the formula $n=T_c/0·9p_c$ (A., 1920, ii, 285), the relation $T_cp_c/d_c^2=$const. is obtained, which should have a value of about $225\times10^3$. This relation was verified for the above 27 liquids, with the exception that acetylene and carbon dioxide give respectively high and low values. It was shown previously (A., 1920, ii, 736) that the relation $d_c=M/9·24z$, where $z$ is the total of the valencies of the atoms in the molecule (C=4, N=3, O=2, H=1), also holds for

non-associated liquids. With the first equation above, this gives $T_c z/M\sqrt{n}=48\cdot7$, which has been verified for a number of aliphatic liquids. In the case of aromatic liquids, the relation holds if the valency of carbon is taken as 3. From Trouton's rule $M.L/T_c=14$, it follows that $Lz/\sqrt{n}=686$, and this is also found to hold for a number of fluids, but aniline and dimethyl*cyclo*hexane give high values. Finally, from the relation $L=0\cdot666p_c/d_c$, it follows that $p_c z/d_c\sqrt{n}=1030$, and this relation is also satisfactorily verified in most cases, but acetylene gives a high value. It is pointed out that these relations can only be tested for relatively simple substances, of which the critical data do not differ widely. Not improbably complications may arise when data are available for other types of substance. E. H. R.

**General Improvement of the Equation of Condition: Special Equation of Condition for Hydrogen.** Léon Schames (*Physikal. Z.*, 1921, **22**, 630—634).—A theoretical paper in which the constants $a$ and $b$ of van der Waals's equation are considered on the basis of a perfectly rigid atom. A general equation of condition is evolved, and taking account of the compressibility of the atoms the equation $pv(1-b/v)+a_0/v(\alpha-v_0/v)=RT$ is deduced for hydrogen. J. F. S.

**Joule-Thomson Effect for Air.** Frederick G. Keyes (*J. Amer. Chem. Soc.*, 1921, **43**, 1452—1470).—The Joule-Thomson coefficients of air have been calculated from the author's equation of state for air based on the measurements of pressure, volume, and temperature by Amagat (*Proc. Nat. Acad. Sci.*, 1917, **3**, 323), and have been compared with the coefficients as measured by Joule and Thomson, by Noell, and by Hoxton. The measurements of Joule and Thomson accord well with the calculations except at zero degrees, whilst the recent careful measurements of Hoxton (*Physical Rev.*, 1919, **13**, 438) exceed the calculated values between 0° and 100° by about 15%. The valne of the ice-point absolute temperature (273·36) deduced from the Chappuis 1000 mm. constant-pressure expansion coefficient for air, corrected by means of the Hoxton Joule-Thomson coefficients is too large, due to the fact that the Chappuis expansion coefficient is too small and the Joule-Thomson values too large. The calculated expansion coefficient and the Hoxton and Joule-Thomson coefficients lead to $T_0=273\cdot197$. The value $T_0=273\cdot135$ is, on the other hand, shown to be substantially correct in that this value is the mean value obtained by graphically extrapolating the measured constant volume and constant pressure expansion coefficients of air, nitrogen, hydrogen, and helium measured at various ice-point pressures. The value 273·135 is also the mean of $T_0$ as deduced from the same data by means of the equations of state for the respective gases. The pressure coefficient at zero of the Joule-Thomson coefficient as obtained by Hoxton is shown to be much larger than that obtained by other observers. The pressure coefficient given by Vogel and Noell (8·8×10[illegible]) is twice that calculated from the equation

($4·5 \times 10^{-4}$) for low pressures, but agrees approximately with that calculated for high pressures, by means of the equation of state. The Bradley and Hale average pressure coefficient to 200 atmospheres at 0° is shown to be $7·3 \times 10^{-4}$, whilst the average value over this range calculated by the equation of state is $7·1 \times 10^{-4}$. The Joule-Thomson coefficient itself at one atmosphere, as given by Vogel and Noell, is 0·277°, and from Bradley's work 0·268°. The equation gives 0·261°. An explanation of the discrepancies in the observed Joule-Thomson numbers is suggested which assumes that at the low pressure surface of the plug a temperature drop is superposed on the Joule-Thomson temperature change due to the momentary persistence of the fine gas streams issuing from the pores of the plug and their subsequent expansion. It is shown that this effect would produce a large apparent pressure coefficient, since the specific effect of the velocity-persistence-effect is shown to vary inversely as the pressure. The value of the measured Joule-Thomson effect at 0° and one atmosphere pressure is given as 0·303 by Hoxton, whilst that deduced from the high pressure measurements of Bradley and Hale is 0·268, as compared with 0·261 calculated by the equation of state. The Joly constant-volume specific heats of air are considered, and it is shown that a correction is required to compensate for the increased specific heat of the copper sphere used by Joly to contain the air. The corrected Joly values are shown to be independent of pressure, which fact confirms the validity of the form of the air equation of state employed. As a further consequence, it is pointed out that at low pressures the Joule-Thomson effect must vary inversely with the absolute temperature. Another important consequence is that the constant volume air thermometer scale reads directly on the absolute scale and therefore requires no correction. J. F. S.

**Simple Methods for the Determination of Melting Points and Critical Temperatures. The Melting Point of Arsenic.** W. HEIKE (*Z. anorg. Chem.*, 1921, **118**, 254).—In a paper under the above title, Rassow (A., 1921, ii, 164) quotes the author's determination of the melting point of arsenic, 830°. The author points out that later work gave a value 814·5°, which is more trustworthy (A., 1916, ii, 248). E. H. R.

**Theory of Concentrated Solutions. Separation of Solids from Organic Mixtures.** J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1921, **30**, 276—290; cf. A., 1909, ii, 388).—From a study of experimental data in the literature relating to the freezing points of binary organic mixtures, it is concluded that deviations from the behaviour of ideal mixtures cannot in all cases be accounted for by assuming combination between the components or polymerisation, as suggested by Dolezalek and others (A., 1909, ii, 22; also Ikeda, A., 1908, ii, 932). It is necessary to take into account also certain physical factors, in the sense of van der Waals's theory, in particular for systems of limited mutual solubility. A provisional scheme of classification of binary organic liquids is based on these chemical and physical factors.

Freezing-point data respecting numerous binary mixtures containing benzene as the crystallising component were compared with the ideal curve obtained by plotting $T$ and $C$ from the thermodynamic equation: $\log_e C = Q(T_0 - T)/2T_0T$, in which $Q$ is the molecular heat of fusion of the component which separates, $C$ is the number of molecules of the latter per 100 molecules of the mixture, $T$ is the temperature at which this component separates, and $T_0$ is the solidifying point of the same substance in the pure state (cf. Washburn, "Introduction to the Principles of Physical Chemistry," 1915, ch. 14). Experimental data for many of the mixtures agreed well with the curve, especially where the two components were closely related and not of widely different chemical character. Deviations from the curve in the direction of the axis of composition might reasonably be attributed to combination between the components, but deviations in the other direction could not in all cases be due entirely to polymerisation, and it is shown that they are to be expected if mixed crystals separate or if the components are not completely miscible in all proportions (cf. Kohnstamm, A., 1911, ii, 93). Similar considerations apply also to boiling-point curves, but abnormalities are here more frequent than with freezing-point curves. In many cases where the boiling-point curve is convex towards the axis of composition (cf. Dolezalek, *loc. cit.*), the assumption of polymerisation sufficient to account for the abnormality appears inadmissible (for example, for carbon tetrachloride, benzene, toluene, etc.), and here again the results may be due to the existence of a range of immiscibility. This explanation was verified in a number of cases, the suspected mixtures separating into two liquid phases when their temperature was lowered sufficiently, by means of liquid air or solid carbon dioxide. J. H. L.

**The Temperature of the Vapour Arising from Boiling Saline Solutions.** George Harker (*J. Roy. Soc. New South Wales*, 1920, **54**, 218—226; cf. Sakurai, T., 1892, **61**, 495).—Experiments with solutions of calcium chloride boiled in a hypsometer either by direct flame or by steam blown in, the only jacketing of the vapour column being by the slightly cooled issuing vapour indicate that the vapour coming from a boiling solution has a higher temperature than the vapour from the boiling pure solvent.
W. G.

**A Simple Receiver for Fractional Distillation under Diminished Pressure.** E. J. Williams (*Chem. News*, 1921, **123**, 265—266).—A simple receiver for fractional distillation under reduced pressure, working on the principle of that of Lothar Meyer, is figured and described. It is constructed with a small distillation flask, a small wide-necked tap funnel, and an adapter. W. G.

**The Separation of Miscible Liquids by Distillation.** Arthur Felix Dufton (T., 1921, **119**, 1988—1994).

**Temperature Correction in Bomb Calorimetry.** N. H. Engström (*Tekn. Tidskr. Kemi Berg.*, 1921, **51**, 18—21).—A formula is evolved for the correction of temperature in bomb calorimetry. This formula is for general use where the tedious calculations by the application of the classical equation of Regnault-Pfaundler is not absolutely necessary. It is given as follows: $k=(1-n)v_1-v$. The order and significance of the letters are the same as in the Regnault-Pfaundler equation. This new formula was tested by a large number of determinations and its error falls within the limits $\pm 0.001$—$0.003°$. The error was seldom as high as $\pm 0.003°$. Chemical Abstracts.

**Constitution and Heats of Combustion.** F. Otto H. Binder (*Chem. Zeit.*, 1921, **45**, 1114—1116; cf. A., 1921, ii, 241, 435).—In continuation of the method previously described (*loc. cit.*) for calculating the heat of combustion of a substance from its constitutional formula, the author has worked out from a consideration of a large number of hydrocarbons the average value of the following: Hydrogen atom attached to carbon 55560, carbon–carbon linking 16258, one carbon valency 24495, compared with 24240, the value obtained by calorimetric experiments on wood charcoal. The heat of combustion of a compound accordingly equals $cH \times 55560 + y \times 24240 + z \times 34170$, where cH is the number of carbon valencies bound to hydrogen, $y$ the number not bound to either hydrogen or oxygen, and $z$ the number of free carbon valencies. From consideration of hydrogen cyanide, cyanogen, and acetonitrile, a mean value for one carbon–nitrogen valency of 35301 cal. is obtained. G. F. M.

**Absolute Value of the Energy of the Linkings between the Atoms of Compounds.** M. Padoa (*Gazzetta*, 1921, **51**, ii, 239—245).—The method of calculation used by Fajans (A., 1920, ii, 354) is substantially that employed by the author (A., 1919, ii, 96), who, however, assumed the value 42 Cal. for the heat of sublimation of diamond and graphite indicated by Thomsen's results, whereas Fajans, on the basis of relationships established by Grüneisen between the heat of sublimation of a solid monatomic element and the ratio of atomic heat to the coefficient of thermal expansion, concluded that the heat of sublimation of carbon is at least 275 Cal. per gram-atom. In spite of the large difference between these two values, both authors conclude that the energy of the linkings between the carbon atoms is almost the same in diamond and in aliphatic hydrocarbons. It seems probable that neither of the above two values is the correct one, and the author considers 150 Cal. to be more nearly the truth; Kohn (A., 1921, ii, 302) arrives at values similar to this. Steiger's results (A., 1920, ii, 355, 735) are also discussed.

Taking the value 150 Cal. for the heat of sublimation of 1 gram atom of carbon and 81·3 Cal. for the heat of dissociation of 1 gram molecule of hydrogen, the energy of the C–C linking is calculated for the aromatic and aliphatic hydrocarbons previously considered.

The results show that the energy of the linking increases froı simpler to more complex compounds. The differences of th values referred to graphite and to diamond vary from 5 to abou 7% and are small considering that the side of the hexagon i $6{\cdot}2\times10^{-8}$ cm. in benzene and $1{\cdot}45\times10^{-8}$ cm. in graphite.

The energy of the simple linking in ethane is 69·9 Cal., that o the double linking in ethylene, 2×59·65 Cal., and that of the tripl linking in acetylene, 3×53·33 Cal. The heat of combustion o acetylene (3 mols.) being 938·4 Cal. and that of benzene vapou 783·3 Cal., the difference between the three triple linkings and th nine simple linkings is 155·1 and that between one triple linking anc three simple linkings hence 51·7 Cal.; the numbers just given foı ethane and acetylene lead to the value 49·7 Cal. The absolute values of the double and triple linkings are, therefore, positive anc unsaturated hydrocarbons all highly exothermic when formec from the free atoms. These considerations have been extendec to various endothermic reactions, such as the formation of hydroger telluride, the formation of cyanogen from carbon and nitrogen the formation of nitrous and nitric oxides, the results indicating that, in all probability, all compounds must be formed from free atoms with generation of heat. T. H. P.

**Compressibility of Benzene, Liquid and Solid.** Theodore W. Richards, Edward P. Bartlett, and James H. Hodges (*J. Amer. Chem. Soc.*, 1921, **43**, 1538—1542).—The compressibility of liquid henzene has been determined at 20°, solid benzene at 0°, and toluene at 0° and 20°, using a steel piezometer previously described (Richards and Bartlett, A., 1915, ii, 229). It is found that the compressibility of solid benzene at 0°, $(\Delta v/\Delta P v_0)_T$, is 0·0000305 over a pressure range 100 to 500 megabars. Incidentally, the compressibility of liquid toluene at 0° over the same pressure range was found to be 0·0000618. A new determination of the compressihility of liquid benzene at 20° confirmed satisfactorily the previous determination made in a glass piezometer (Richards and Shipley, A., 1916, ii, 376), giving the value 0·00007207 for the same range. The compressibility of solid benzene is shown to be less than half that of liquid henzene at the same temperature. Thus another case, supporting the majority of those investigated, is found in which the solid shows a much smaller compressibility than the liquid (A., 1915, ii, 518). No interpretation of this result is offered at present. J. F. S.

**Relative Volumes of the Chemical Elements.** Hawksworth Collins (*Chem. News*, 1921, **122**, 76—77, and **123**, 95—97).—A continuation of previous work (A., 1921, ii, 168). In the first part, a table is given of the relative volumes and the densities of a number of organic compounds, the latter quantity is compared with the experimentally determined values. The calculated results are based on the hypothesis previously put forward by the author. In the second part, a further long list is given. It is shown that the experimental facts obtained from the examination of 76 mole-

ules demonstrates that one relative volume of hydrogen is 15·25 at 15° whether, Cl, Br, I, $NH_2$, $NO_2$, SH, $C_2H_3$, $C_2H$, $CO_2Me$, $CO_2Et$, $CO_2Pr$, $CO_2H$ or —OH be displaced; in this case —OH=13·29. In a further series of 24 compounds, the relative volume of hydrogen is 12·22 at 15° for the same replacements, OH=10·21. The methyl group has a volume 31·67 at one end of a chain and 28·64 at the other end. When an atom of hydrogen the volume of which is 15·25 is displaced by methyl, the volume of the latter is 31·67, and when the displacement occurs with hydrogen 12·22, the volume of the methyl is 28·64. The two valencies of carbon concerned are distinguished by the fact that one (first position) has hydrogen with a volume 15·25 and the other (second position) has hydrogen with a volume 12·22. J. F. S.

**Atomic and Molecular Volumes at the Absolute Zero. II.** W. HERZ (*Z. anorg. Chem.*, 1921, **119**, 221—224).—In a previous paper it was shown by Lorenz and Herz (A., 1921, ii, 536) that the molecular volumes of alkali salts reduced to absolute zero are smaller than the sums of the volumes of the constituent atoms, similarly reduced according to the law of corresponding states. The inquiry has been extended to a number of simple inorganic compounds other than salts. In the hydrogen compounds the molecular volume is smaller than the sum of the atomic volumes, but the difference becomes smaller with increasing molecular weight. In the halogen acids, for example, these differenees are, HF, 7·52; HCl, 3·09; HBr, 1·09; HI, 0·01. In the trihaloids of the elements of the fifth group, however, the molecular volume is greater than the sum of the atomic volumes. The molecular volumes are also calculated from the dielectric constant by the Clausius-Mossotti equation $\gamma=D-1/D+2.M/d$. The values obtained are sometimes greater and sometimes smaller than the actual molecular volumes. The divergences may be due to association in the liquids. E. H. R.

**Surface Tensions and Densities of Liquid Mercury, Cadmium, Zinc, Lead, Tin, and Bismuth.** THORFIN R. HOGNESS (*J. Amer. Chem. Soc.*, 1921, **43**, 1621—1628).—The densities of liquid zinc, cadmium, tin, lead, and bismuth have been determined at various temperatures and the following values obtained: zinc $d=6·59—0·00097(t-419)$, lead $d=10·71—0·00139(t-327)$, cadmium $d=8·02—0·00110(t-320)$, bismuth $d=10·07—0·00125(t-269)$, and tin $d=7·01—0·00074(t-232)$. The surface tension for mercury and the above-named molten metals has been determined by the Cantor drop pressure method for a series of temperatures. The values of the surface tension may be calculated by the following equations: mercury $\tau=467—0·043(t+39)—0·000386(t+39)^2$, bismuth $\tau=378—0·063(t-269)$, cadmium $\tau=630—0·065(t-320)$, lead $\tau=444—0·077(t-327)$, tin $\tau=531—0·080(t-232)$, and zinc $\tau=758—0·090(t-419)$. It is shown that there is no appreciable difference between the surface tensions of mercury in dry air, hydrogen, and a vacuum. J. F. S.

**Relationship of the Internal Friction of Organic Liquid to other Properties.** W. HERZ (*Z. Elektrochem.*, 1921, 27, 518—521).—In the case of a large number of simple non-associated organic liquids an approximately constant relationship exist between the surface tension and the critical pressure. This relationship is $\gamma_s : p_c \simeq 1{\cdot}6\times10^4$, in which $\gamma_s$ is the surface tension at the boiling point and $p_c$ the critical pressure. Between the surface tension and the internal friction ($\eta_s$), both at the boiling point, the approximate relationship $\gamma_s : \eta_s \simeq 6\times10^3$ exists. It is also shown that the two expressions, $M\gamma_s/T_s d_s$=const. and $Ld_s/\gamma_s$=const., both hold for non-associated organic liquids, where $M$ is the molecular weight, $L$ the latent heat of vaporisation, and $d_s$ the density at the boiling point $T_s$. In the case of the former equation, the constant value varies between $6{\cdot}7\times10^4$ and $11{\cdot}3\times10^4$, whilst in the latter the value is between $2{\cdot}0\times10^4$ and $3{\cdot}2\times10^4$. Two relationships connecting the internal friction and the critical temperature respectively with the molecular refractivity are deduced. These have the form $\eta_s MR/T_c$=const. and $\eta_s MR/T_s$= const., where $MR$ is the molecular refractivity. The constant in the first case varies between $1{\cdot}1\times10^{-4}$ and $1{\cdot}7\times10^{-4}$ and in the second case between $1{\cdot}6\times10^{-4}$ and $3{\cdot}2\times10^{-4}$. If $n$ is the number of atoms in a non-associated liquid, the quantity $\eta_s n/T_s$ is constant and has a value between $0{\cdot}86\times10^{-4}$ and $1{\cdot}39\times10^{-4}$. Finally, it is shown that $V_c\eta_s/T_s$ and $V_c\eta_s/T_c$ are both constant for the same class of organic liquid. In the first case the value varies between $9{\cdot}0\times10^{-8}$ and $12{\cdot}6\times10^{-8}$, and in the second case between $5{\cdot}8\times10^{-8}$ and $8{\cdot}0\times10^{-8}$. J. F. S.

**Theory of Brownian Movement.** GUSTAV JÄGER (*Sitzungsber. K. Akad. Wiss. Wien*, 1919, [2a], **128**, 1271, 1298; from *Chem. Zentr.*, 1921, iii, 833).—Stokes's law is held to be inapplicable in the case of Brownian movement. It is shown from consideration of mechanical examples that if this law holds, osmotic pressure must be exerted as a continuous force and the consequences of Einstein's equation for Brownian movement and the calculation of molecular size from diffusion are justified. The distribution of energy for particles of any number of molecules may be obtained from Maxwell's law directly by gradual building up of groups from molecules. The velocity of particles relative to the liquid medium, including their Brownian movement, is only to a small degree dependent on their mass. G. W. R.

**Influence of Water-content on the Adsorption-capacity of an Active Charcoal.** HEINRICH HERBST (*Biochem. Z.*, 1921, **118**, 103—119).—The highest adsorption is obtained with dry charcoal. For practical purposes 10% of water is not harmful, since the presence of water has a catalytic effect. H. K.

**Absorption of Gases by Crystals.** R. SEELIGER and K. LAPKAMP (*Physikal. Z.*, 1921, **22**, 563—567).—Partly or completely dehydrated zeolites have the power of absorbing gases in large quantities. The absorption of a mixture of neon and helium,

nitrogen, oxygen, methane, nitric oxide, carbon dioxide, acetylene, hydrogen, and ammonia by dehydrated chabasite ($CaAl_2Si_4O_{16},6H_2O$) has been examined at 0° under a series of pressures from 0° to 760 mm. It is shown that, with the exception of hydrogen, the amount of gas absorbed is greater the higher the critical temperature of the gas. The following volumes of gases in c.c./gram of chabasite at 0° and 760 mm. are absorbed. Neon 25% + helium 75%, 4·10; nitrogen, 6·89; oxygen, 8·32; methane, 15·18; nitric oxide, 25·67; carbon dioxide, 39·60; acetylene, 56·46; hydrogen, 82·22, and ammonia, 180·59. The adsorption curves can be approximately reproduced by the formula $v=\alpha p^{1/n}$, in which $\alpha$ and $1/n$ are constants. All gases except nitric oxide, ammonia, and impure acetylene can be entirely removed from the crystals by lowering the pressure. The results do not indicate whether the absorhed gases are adsorbed according to the usual conception of the term, or whether they enter into the structure of the crystal lattice. In favour of the pure adsorption are the qualitative character of the adsorption isotherm, the connexion between the critical temperature and the amount of absorption, and the effect of reducing the pressure. Further, the connexion between $1/n$ and the critical temperature also indicates a pure adsorption. On the other hand, the large absorption of hydrogen and the difficulty experienced in removing nitric oxide, ammonia, and impure acetylene from the crystals point to the view that the absorbed gases enter into the crystal lattice in the position occupied by the water before dehydration. J. F. S.

**Graphic Deductions with regard to the Dissociation of Weak Electrolytes.** N. SCHOORL (*Rec. trav. chim.*, 1921, **40**, 616—620).—An expression is deduced from Ostwald's dilution law which gives approximately correct values for the degree of ionisation of weak electrolytes. Such approximation is depicted graphically in contrast with the calculated values. H. J. E.

**The Redissolution of a Salt during the Isothermal Evaporation of a Solution.** ETIENNE RENGADE (*Compt. rend.*, 1921, **173**, 1080—1081; cf. A., 1921, ii, 93).—A reply to Raveau (cf. A., 1921, ii, 682). W. G.

**Formulæ for the Solubility of certain Salts in Aqueous Ethyl Alcohol and Water.** W. D. TREADWELL (*Helv. Chim. Acta*, 1921, **4**, 982—991).—Attempts are described to devise a mathematical expression for the diminution of the solubility of a salt in water by the addition of alcohol on the assumption that the solvent action is exerted by the water alone, and that its extent is lessened by its dilution with the alcohol. Consideration is confined for the present to substances which are almost insoluble in absolute alcohol. In these circumstances, the solubility is expressed by the equation $h=L_0C_w^2k$, in which $L_0$ is the solubility of the salt in pure water, $C_w$ the concentration of the water in the solvent, and $k$ a proportionality factor of the approximate order, 1. The results calculated from this formula ($k=0·88$) are in harmony with the experimental data for the solubility of potassium chlorate in

mixtures of alcohol and water at the atmospheric temperature at 30°, and at 40°. The influence of temperature, therefore, is manifest essentially in the alteration of the value, $L_0$. Within certain limits of alcoholic concentration, similar observations are made with potassium nitrate, but, in this case, the value of $k$ does not appear to be so independent of the temperature. At 14·5° the solubility of potassium chloride is represented satisfactorily by the expression when $k=0·93$, but at 30° and 40° a distinct specific action of the alcohol is observed which causes a variation in the value of $k$ with varying alcoholic content of the solution. This specific action is also in evidence in the cases of sodium chloride, etc., more noticeably, of ammonium sulphate.

The remarkable independence of the value of $k$ of the temperature in the case of potassium chlorate and, to a more limited extent, in that of potassium nitrate points to the conclusion that alcohol behaves merely as an inert diluent. $L_0$ may therefore be expressed as a function of the temperature and replaced by the expression $aK^n$ in which $a$ and $n$ are empirical constants and $K$ is the ionisation product of water $\times 10^{14}$. The solubility of potassium chlorate in any mixture of alcohol and water between 12° and 40° is given by the expression: $L=8·4\times K^{0·482}.C_w^2\times 0·88=7·4·K^{0·482}\times C_w^2$. That of potassium nitrate, sodium chloride, potassium chloride, potassium sulphate, and lead nitrate can be calculated satisfactorily if a constant value is given to $n$, but, in the case of sodium chloride a distinct linear variation of the exponent is noticeable which, if taken into consideration, permits a very exact calculation of the observed values. The solubility of non-ionised mercuric chloride cannot be calculated accurately if $n$ is assumed to be constant. H. W.

**Application of Ideal Solution Equations to Dilute Aqueous Solutions.** JAMES KENDALL (*J. Amer. Chem. Soc.*, 1921, **43**, 1391—1396).—A theoretical paper in which it is shown that the present method of applying the fundamental ideal solution equation to dilute aqueous solutions, particularly in the vapour pressure and freezing-point depression equations, leads to certain incompatibilities, which have been pointed out and discussed. It is also shown that the discrepancy disappears when due notice is taken of the fact that the vapour pressure of water at the ordinary temperature must be ascribed practically entirely to its uni-molecular fraction, the shift in the equilibrium $(H_2O)q \rightleftharpoons qH_2O$ on addition of a solute counterbalancing the effect of the association on the molecular fraction. Some fundamental errors in the present application of ideal osmotic pressure and freezing-point depression equations to dilute aqueous solutions have also been pointed out and corrected. J. F. S.

**Factors Affecting the Stability of Additive Compounds in Solution and their Influence on Ionisation Equilibria. I.** JAMES KENDALL and PAUL M. GROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 1416—1426).—In an earlier paper (Kendall, Booge, and Andrews, A., 1918, ii, 36, 37), it is postulated that the formation of solvent-

olute complexes is a pre-requisite to ionisation in solutions. On this assumption, it should be possible to predict the degree of dissociation in any given solution from (*a*) the stability of the complexes with respect to their components, and (*b*) the instability of the complexes with respect to their ionisation products. The first of these points has been dealt with in detail in previous papers (*loc. cit.*), and the rules formulated have here been extended to the association of pure liquids. In the present communication the study of the second point—the factors affecting the ionic disintegration of solvent–solute complexes in solution—has been commenced. These generalisations are shown to be in excellent qualitative agreement with the experimental data of earlier investigators. A more stringent test of their validity is furnished by careful conductivity determinations on specially selected systems (cf. following abstract). The connexion between the ionisation hypothesis presented here and the views of Abegg and Bodländer, on the one hand, and of Werner, on the other, has been shortly examined and some points of difference have been indicated.

J. F. S.

**Compound Formation and Specific Conductivity in Solutions of the Types, Acid–Ester, Acid–Ketone, and Acid–Acid.** JAMES KENDALL and PAUL M. GROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 1426—1439).—Complete specific conductivity–composition curves have been produced for fourteen systems of the types, acid–ester, acid–ketone, and acid–acid, at 25°. The substances employed are all liquids, and the specific conductivity of these was taken as the test of purity. It is shown that this property is far more sensitive to small amounts of impurities than the melting point or boiling point; the specific conductivity at 25° is found for the substances named to be: ethyl acetate, $<1\times10^{-9}$; ethyl benzoate, $<1\times10^{-9}$; benzyl benzoate, $<1\times10^{-9}$; acetone, $\cdot8\times10^{-8}$; acetophenone, $5\cdot5\times10^{-8}$; acetic acid, $2\cdot4\times10^{-8}$; propionic acid, $<1\times10^{-9}$; monochloroacetic acid, $1\cdot4\times10^{-6}$ (60°); trichloroacetic acid, $6\cdot2\times10^{-9}$ (60°), and formamide, $4\times10^{-6}$. These results are from one-third to one-six hundred and twentieth of the previous best values. The conductivities of solutions of the above-named types are, in general, considerably in excess of those of the pure components, and increase uniformly with increasing diversity in character (that is, in the positive or negative nature of the constituent radicles) of their components. The results obtained have been correlated with those derived from freezing-point measurements on similar systems, and the validity of the fundamental relationships between compound formation and ionisation in solutions (see preceding abstract) has been confirmed. The maximum specific conductivity in no case corresponds with a composition of the system which is the same as that of an isolated compound. The following compounds have been isolated: $CCl_3\cdot CO_2H,CH_3\cdot CO_2Et$, m. p. −27°; $CCl_3\cdot CO_2H,C_6H_5\cdot CO_2Et$, m. p. −23°; $CCl_3\cdot CO_2H,C_6H_5\cdot CO_2\cdot C_7H_7$, m. p. 11·9°; $CCl_3\cdot CO_2H$,COMePh, m. p. 26°; $H\cdot CO\cdot NH_2,2CH_3\cdot CO_2H$, m. p. −8°.

J. F. S.

**Prediction of Solubility in Polar Solutions.** JAMES KENDALL, ARTHUR W. DAVIDSON, and HOWARD ADLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1481—1502; cf. preceding abstracts).—The various factors inducing deviations from the ideal solubility curve in polar solutions have been critically discussed, and it has been shown that the predominant disturbing factor is additive compound formation between the components of the solution. In previous papers (*loc. cit.*) it has been shown that the extent of such compound formation in any series is dependent on the diversity in character of the constituent radicles of the components, the basis of the diversity being the relative position of the variable radicles in the *E.M.F.* series. Ionisation, furthermore, has been found to increase uniformly with compound formation. These generalisations have been employed to predict solubility relationships in systems of various types. It has been shown that: (*a*) for a given solute in a series of different solvents, increasing solubility and increasing compound formation proceed in parallel, (*b*) for a series of different solutes of high melting point in a given solvent, increasing solubility and increasing compound formation also proceed in parallel at low temperatures. Illustrations of these rules for non-aqueous and aqueous solutions have been presented which indicate their agreement with the facts of experiment. A general discussion of solubility relationships in systems of increasingly complex nature (for example, RX—HX; RX—$H_2O$; RX—R′X—$H_2O$) has been made, and the rules deduced for the simpler types of systems have been found to be applicable, to a limited extent, to the more complex types. For example, (*a*) salts of a very weak base exhibit increasing hydrate formation and increasing solubility in water as the acid radicle X diverges from OH′; salts of a very weak acid show the same behaviour as R diverges from H. (*b*) The increase in the solubility of a sparingly soluble salt in water on addition of a second salt containing a common ion, due to complex salt formation, is dependent on the diversity of the variable radicles.

J. F. S.

***Solubilities of Acids in Aqueous Solutions of other Acids.*** JAMES KENDALL and JAMES C. ANDREWS (*J. Amer. Chem. Soc.*, 1921, **43**, 1545—1560; cf. preceding abstracts).—Solubility curves have been produced for hydrogen sulphide, boric acid, benzoic acid, and salicylic acid in aqueous solutions of hydrogen chloride of a series of concentrations and also for the same acids, except hydrogen sulphide in aqueous solutions of nitric acid. The changes of the specific conductivity of the solvent acids, due to the presence of the weaker acids in solution, has also been investigated. The results obtained, together with those of previous investigators, have been critically discussed in connexion with the rule established previously (*loc. cit.*), that compound formation between acids in pairs increases in extent with increasing diversity of acidic strength. The predicted and observed solubility curves for systems of various types have been compared, and satisfactory agreement, in general, has been obtained. The conductivity results also fall into line in

most cases. Certain abnormalities, however, do appear in particula systems, which are probably to be explained by the water enterin into the equilibria in some as yet undefined way. J. F. S.

**The Influence of Pressure on Spontaneous Crystallisation** MEINHARD HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 353—364).— Experiments were made to determine the influence of pressure o the number of nuclei developed during spontaneous crystallisatio at different temperatures (cf. Tammann, A., 1898, ii, 330). Ex periments were made with betol, piperine, and papaverine, and i *was found that increased pressure, up to 1000 kilos. per sq. cm* had the same effect on nuclei formation as on melting point. A 1000 kilos. the m. p. of betol is raised from 93° to 122·9°, and th temperature of spontaneous crystallisation was raised by a closel corresponding amount. In the case of piperine, the temperatur of maximum formation of nuclei was raised from 35° to 70° b increasing the pressure from 1 to 1000 kilos. per sq. cm., and in th case of papaverine from 40° to 60°. The form of the curve showin the variation of number of nuclei with temperature was simila at both pressures. The maximum number of nuclei is double at the higher pressure in the case of piperine, but in the case c papaverine it is about the same at 1 kilo. and 1000 kilos. per sq. cn
E. H. R.

**Crystallisation Velocity under High Pressure.** MEINHAR HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 325—352).—The cor ditions determining crystallisation velocity at normal pressur have been recorded by Tammann (A., 1898, ii, 425; 1899, ii, 27 548). For examining the effect of pressure on crystallisatio velocity, a modified form of an apparatus described by Tamman was used ("Kristallisieren und Schmelzen," p. 165). The substance studied were thymol, phenyl salicylate, benzophenone, apiole, ca cium nitrate tri- and tetra-hydrates, cadmium nitrate tetrahydrat mixed crystals of calcium and cadmium nitrates, guaiacol, form anilide, benzoic anhydride, *m*-iodonitrobenzene, and benzylanilin In general, the effect of pressure, up to 2000 kilos. per sq. cn was remarkably small. In two cases there was an increase i crystallisation velocity of 43% and 18% respectively, but in mo cases a slight fall, the greatest being 49% at 1000 kilos. per s cm. As the increased pressure has also the effect of raising th melting point considerably, for instance by 27·4° at 1000 kilos. in th case of phenyl salicylate, and the crystallisation temperature limi are raised proportionately, it can be concluded that the real effect o pressure alone is always to decrease the maximum crystallisatio velocity. The influence of other substances on the crystallisatic *velocity of benzophenone was not appreciably affected by pressur*
E. H. R.

**Recrystallisation Produced by Annealing.** PAUL GAUBER (*Compt. rend.*, 1921, **173**, 1089—1092).—From a study of the be haviour of crystals of vanillin at a temperature slightly below the melting point and of substances like paraffin wax or cetin, whic

give malleable crystals in the neighbourhood of their melting point, it is shown that recrystallisation is, as a rule, only possible if the crystals are sufficiently malleable for certain mechanical actions to modify their crystalline system. There is then produced, as it were, a slow polymorphic transformation, with, however, this difference, that in hammer-hardened substances there may remain some intact crystals which will act as nuclei to start the recrystallisation. W. G.

**Crystal Structure and Atomic Constitution. I.** P. NIGGLI (*Z. Kryst. Min.*, 1921, **56**, 12—45; from *Chem. Zentr.*, 1921, iii, 833—834).—A discussion of the bearing of crystal structure on atomic constitution in the light of existing crystallographic data. Crystal symmetry with a known arrangement of atoms in the lattice implies also a certain minimal symmetry in the structure of the component atoms. A volume effect must follow from the actual effective size of atoms, as, for example, in the series formed by the carbonates of calcium, magnesium, ferrous iron, nickel, and cobalt, all of which have the calcite structure. From a consideration of published crystallographic data, the univalent metallic elements may be arranged in two series, namely, a principal series, lithium, sodium, potassium, rubidium, and cæsium and a subsidiary series, copper (univalent), silver, and gold (univalent). Molecular volume does not increase continuously with electron number but shows periodicity. Similar results are given by bivalent and tervalent metallic elements. With higher valencies the periodicity in molecular volumes tends to disappear (cf. Bragg, A., 1920, ii, 537). G. W. R.

**Crystal Structure and Atomic Constitution. II.** P. NIGGLI (*Z. Kryst. Min.*, 1921, **56**, 167—190; from *Chem. Zentr.*, 1921, iii, 834—835).—A continuation of an earlier discussion (see preceding abstract) of the relations between crystal structure and atomic constitution. The theories of Kossel, Vegard, Lewis, Langmuir, Lacomble, and Kohlweiler imply certain assumptions as to atomic structure. The periodicity in atomic volumes already noted is related to the arrangement of electrons in the atom. Whilst crystal form is connected with chemical constitution, isomorphism in its widest sense is a geometrical rather than a chemical effect. A comparison of the volume relationships in series of crystalline "isosteric" compounds permits a comparison of the effective sizes of atoms of differing valency, whereby it appears that atomic size diminishes with increase of valency. G. W. R.

**Investigation of Crystal Space Lattices by means of Röntgen Rays: a Simple Röntgen Tube.** WALTER GERLACH (*Physikal. Z.*, 1921, **22**, 557—559).—The lattice constant, *a*, has been determined for magnesium oxide, calcium oxide, strontium oxide, and barium oxide. In all cases the substances are shown to be regular and belong to the sodium chloride type. The values recorded are MgO, 4·204; CaO, 4·762; SrO, 5·100; BaO, ... Making use of the Debye-Scherrer method, it is shown that ...

the ions of magnesia are both bivalent. The lattice of fluorspar *has been redetermined and the structure put forward by Bragg* confirmed. The lattice constant is found to be $a = 5{\cdot}452$ Å.U. $\pm 0{\cdot}2\%$. Various forms of silicon have been examined and shown to be crystallographically similar. The lattice is of the diamond type and has the constant $a = 5{\cdot}400 \times 10^{-8}$ cm. $\pm 0{\cdot}2\%$. The transport of anti-cathode material towards the cathode has been considered. It is shown that after using a Siegbahn-Hadding tube for a prolonged period a deposit of the anti-cathode material is found on the cathode in the form of small crystals. In the case of aluminium cathodes, the crystals were well-formed cubes of 1 mm. edge. In the case of copper cathodes the transport of material takes place in the ionic form, and is not in any way to be regarded as a distillation. The amount of material transported is in accordance with the dimensions of the ionic stream.

A Röntgen tube is described in which a portion of the outside wall serves as the metallic hemisphere constituting the cathode, whilst the anti-cathode is situated at the geometrical centre of the hemisphere. The Röntgen rays pass through a number of holes in the cathode which is rendered air-tight by suitable cements.

J. F. S.

**The Theory of Resistance Limits in Mixed Crystals.** G. Masing (*Z. anorg. Chem.*, 1921, **118**, 293—308).—It has been held by Tammann (A., 1919, ii, 398) that the existence in binary mixed crystals of resistance limits to the attack of chemical agents which react with one constituent but not with the other provides a proof that the two kinds of atom in the mixed crystals are regularly distributed on a space lattice. The author shows that, making certain assumptions, it can be proved by the mathematical laws of probability that resistance limits will occur if the atoms are irregularly distributed on the space lattice. The limits calculated are not the same as those found experimentally, but they depend on certain simple arbitrary assumptions made with respect to the manner in which the solvent attacks the mixed crystals, and these may be insufficient. The work is only intended to show that the mere existence of resistance limits is no proof of the regular distribution of the atoms in the mixed crystals.

E. H. R.

**Coagulation of Colloids by Electrolytes.** Humphrey D. Murray (*Chem. News*, 1921, **123**, 277—279).—A general review of the work within recent years on the coagulation of colloids by electrolytes. J. F. S.

**Kinetic and Static Coagulation Measurements of Suspensoids.** Friedrich Vincenz von Hahn (*Z. Elektrochem.*, 1921, **27**, 501—505).—A general discussion of the various kinetic and static methods of measuring the coagulation of suspensoids with the object of ascertaining the suitability or otherwise of these methods for determining the relative stability of the sols. A new method of determining the stability by coagulation is described.

The apparatus consists of a long U-tube consisting of a narrow tnbe and a wide tube; the wide tube terminates at its lower end in a tap and extends slightly beyond the cross-piece joining the two tubes which is closed by a tap. In making a determination, the tap is closed and the wide limb filled with water and the narrow tube with the sol, both to the same height. Tbe tap is now opened, and the levels adjust themselves; if now a portion of the disperse phase owing to coagulation reaches the continuation of the longer tube, tbe density of the sol is changed and the meniscus commences to move. The time which must elapse before this movement of the meniscus begins is characteristic of the stability of the sol. Two other, rather more sensitive, methods based on the same principles are described. J. F. S.

**The Equilibrium in the Reduction of Nickel Chloride by Hydrogen.** E. BERGER and G. CRUT (*Compt. rend.*, 1921, **173**, 977—979).—Within wide limits the equilibrium of the reversible reaction $NiCl_2+H_2 \rightleftharpoons Ni+2HCl$, is determined accurately by the formula $29642/4{\cdot}571T-1{\cdot}75 \log T-0{\cdot}006T^2/4{\cdot}571+\log p+\log [\alpha^2/(100-\alpha)]=K$, taking the heat of reaction from left to right as −30700 cal. at 15° and the value of $K$ as 5·93. The equilibrium concentrations are the same in whichever direction the reaction proceeds. W. G.

**An Explanation of Liesegang's Rings.** HUGH McGUIGAN (*Science*, 1921, **54**, 78—80).—When a minute drop of silver nitrate solution is placed on a gelatin gel containing potassium dichromate, there is an immediate formation of a circle of silver chromate about which is a sharply demarcated zone of influence from which the chromate has been removed. The Liesegang ring formation when a larger drop of silver nitrate is used is explained as follows: Silver chromate is formed and a clear zone results in the gelatin by the attraction of the chromate to the silver. Beyond this zone of influence, the chromate is fixed and remains so unless an attraction force is exerted. The silver nitrate now wanders on through the ring into the clear zone until it is sufficiently close to the chromate gelatin to exert an attraction which again draws the chromate and forms another ring and clear zone. At the same time the chromate exerts a "pull" on the silver and the ring is formed where the forces are balanced. Again it may be presumed that to start the chromate moving will require a greater force than to keep it moving after the movement has commenced; consequently the second ring is separated from the first. With each succeeding ring the concentration of the silver is less and this also will operate to remove the succeeding rings farther apart. As a requisite for ring formation the precipitate formed must be permeable to the liquid solution used, in this case silver nitrate. CHEMICAL ABSTRACTS.

**Preparation of Nitroanisole from Nitrochlorobenzene.** A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 1029—1035).—The action of *o*- or *p*-nitrochlorobenzene on sodium methoxide in the presence

of methyl alcohol has been studied and by a combination of different titrations it has been possible to determine the rate of formation of each component of the change (cf. A., 1921, ii, 497). Below 70°, the reducing action of intermediately formed alkoxide is so slight as to be practically negligible. The yields of nitrophenol ethers and the rate of reaction depend, not only on temperature and time, but also on the quantity and composition of the solvent. Accelerating factors increase the yield of ethers if they do not *also* accelerate the subsidiary reactions. High alcoholic concentration and a minimum amount of solvent are favourable in this respect. The use of temperatures higher than 70° or of a large excess of alkali is disadvantageous on account of the increased production of dichloroazoxybenzene or nitrophenol. The possibility of the hydrolysis of the ether formed need not be taken into account, and the whole of the alkali may therefore be added at the commencement of the operation. H. W.

**The Theory of Reaction Velocities.** N. R. Dhar (*Z. anorg. Chem.*, 1921, **119**, 177—178).—In criticising Lewis's theory, Lindemann (A., 1920, ii, 743) states that the inversion of sucrose by acids, which should proceed $10^{13}$ times as fast in sunlight as in the dark, is not accelerated at all by light. The author has found that a solution of sucrose in tropical sunlight is completely inverted even in absence of acids, whilst in presence of hydrochloric acid the inversion is distinctly accelerated by sunlight. These observations therefore confirm the theory of Lewis in a qualitative manner. Reactions which have a large temperature coefficient are those most sensitive to light. E. H. R.

**Rates of Hydrolysis of the Rare Earth Carbonates and the Serial Order of the Rare Earth Elements.** Paul H. M.-P. Brinton and C. James (*J. Amer. Chem. Soc.*, 1921, **43**, 1446—1451).—The relative rates of hydrolysis of the carbonates of ytterbium, thulium, yttrium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, praseodymium, lanthanum, and cerium have been determined. An equivalent quantity of the carbonate of each of the earths was dissolved in a definite quantity of water and treated with the theoretical quantity of sodium carbonate and boiled. The carbon dioxide evolved was collected during half-hour periods and measured, and from the results the percentage hydrolysis calculated. In the case of lanthanum and cerous carbonate anomalous behaviour is displayed inasmuch as the whole of the carbon dioxide is evolved in the first half-hour and consequently on plotting percentage hydrolysis against the time of boiling they give horizontal line curves, whilst the curves for the other elements are slowly rising curves, slightly convex to the time axis. The curves place the elements, with the exception of the two named, in the order of their basicity. The position thus assigned to yttrium agrees with the solubilities of its compounds, whilst previous determinations of basicity have not done so. The increasing order of basicity of the ten elements concerned

is given as: ytterbium, thulium, yttrium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, and praseodymium. A short discussion on the serial order of the rare earth elements is given. J. F. S.

**The Explosion of Acetylene and Nitrogen. I.** William Edward Garner and Kichimatsu Matsuno (T., 1921, **119**, 1903—1914).

**Velocity of Decomposition of Mono- and Di-substituted Malonic Acids.** August L. Bernoulli and Heinrich Jakubowicz (*Helv. Chim. Acta*, 1921, 4, 1018—1029).—In extension of the work of Bernoulli and Wege (A., 1919, ii, 503), the rate of decomposition of malonic, diallylmalonic, diethylmalonic, phenylmalonic, benzylmalonic, ethylmalonic, tartronic, mono- and di-chloromalonic, and dibromomalonic acid has been measured at a variety of temperatures.

The relative effect of the different substituents as established by Bernoulli and Wege (*loc. cit.*) at 100° is found to be maintained at all temperatures investigated. As mono-substituents, bromine, chlorine, and hydroxyl accelerate the decomposition of malonic acid in order of decreasing effect. The temperature curves of the mono-substituted acids diverge from one another with increasing temperature, without, however, intersecting. The temperature curves of the di-substituted malonic acids (from 80° upwards) remain parallel to one another and to that of malonic acid so that the latter behaves as "symmetrically di-substituted." Two similar substituents depress the rate of decomposition greatly, even when the latter is accelerated by the same substituent acting singly. The retarding action becomes more marked with increase in mass of the substituent; this is particularly noticeable with dibromomalonic acid. The effect of substitution in the case of di-substitution is the result of two component actions, (*a*) a specific effect which is obvious in the case of mono-substitution, and (*b*) a symmetry effect which depends on the mass and not on the electrochemical character of the radicle or atom. H. W.

**Influence of Neutral Salts on the Hydrolysis of Ethyl Formate.** Alexander Bernard Manning (T., 1921, **119**, 2079—2087).

**The Maximum Stability of Esters of Carboxylic Acids.** Karl Gustav Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69—96).—Experiments were made to determine the influence of hydrogen-ion concentration on the stability of methyl acetate and ethyl acetate. The experiments were carried out at 85·55° and 75·40°. The ester was heated in aqueous solution in presence of a "buffer" salt (sodium acetate) in a sealed quartz tube for a known time. The hydrogen-ion concentration was determined by direct measurement before and after the experiment and the amount of hydrolysis was determined by titration with barium hydroxide solution. The velocity constant was calculated from the usual unimolecular equation. In the case of methyl acetate, the lowest velocity con-

tant, that is, the greatest stability, was found at 85·55° with $P_H$=4·70, and in the case of ethyl acetate, $P_H$=5·1. The presence f neutral salts, sodium chloride, or potassium nitrate had no effect n the position of the point of maximum stability. The curves btained by plotting the velocity constants as ordinates against he $P_H$ values descend to a minimum at the $P_H$ representing maximum stability, but they are not symmetrical about this point, rising nore steeply on the alkaline side. It follows that H- and OH-ons cannot have the same hydrolytic activity (cf. Wijs, A., 1893, ., 364; 1894, ii, 82). What function the reaction velocity is of he H- and OH-ions cannot yet be determined. Neutral salts ncrease the reaction velocity in alkaline solution, that is, when $P_H$ is high, by increasing the acidity, but on the acid side of the oint of maximum stability they have much less effect.

E. H. R.

**Preparation and Hydrolysis of Benzyl Esters.** E. H. Volwiler and E. B. Vliet (*J. Amer. Chem. Soc.*, 1921, **43**, 1672—676).—The comparative rates of hydrolysis of certain benzyl sters were determined in order to obtain a basis for the correlation f chemical properties and physiological action. The rates of ydrolysis of these benzyl esters increase in the following order: alicylate, benzoate, stearate, cinnamate, acetate, succinate, and umarate. The rate of hydrolysis of the benzyl group in benzyl ceto-oxybenzoate is of the same order as in benzyl salicylate.

W. G.

**The Influencing of Catalysts and Specifically Active Catalysts.** Karl W. Rosenmund and Fritz Zetzsche (*Ber.*, 921, **54**, [*B*], 2885—2888; cf. A., 1921, ii, 320, 392, 393).—A eply to the criticism of Abel (A., 1921, ii, 542). H. W.

**Catalytic Action at Solid Surfaces. VII. Influence of Pressure on the Rate of Hydrogenation of Liquids in the Presence of Nickel.** E. F. Armstrong and T. P. Hilditch *Proc. Roy. Soc.*, 1921, [*A*], **100**, 240—252; cf. A, 1921, ii, 582; 920, ii, 608).—The influence of pressure on the rate of absorption f hydrogen by pinene, ethyl cinnamate, ethyl linoleate, linolein, nolenin, geraniol, terpineol, oleic acid, citral, and carvone in the resence of nickel has been investigated. The results fall into hree definite groups: (i) *Normal.* In the absence of substituent roups of the type mentioned below and in the presence of sufficient ickel (generally as long as at least 0·1% of nickel is present) the thylenic union is hydrogenated at a rate which is in almost exact roportion to the absolute pressure of the hydrogen. To this roup belong ethyl cinnamate, ethyl linoleate, and pinene. (ii) *Subnormal.* At very low concentrations of catalyst (for example, ·01—0·02% of nickel calculated on the organic compound) the ncrease in the rate of hydrogenation becomes less than proportional o the increase in pressure. The compounds which absorb hydrogen ost readily are in general more prone to show the sub-normal ffect when the concentration of the catalyst is diminished, and it

is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic or linolenic acid or citral, although at low concentrations of catalyst it is also shown by ethyl cinnamate. (iii) *Abnormal.* If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), it is found that increase in hydrogen pressure causes an increase in the rate of hydrogen absorption in greater than simple proportion to the altered concentration of the hydrogen. This is observed with unsaturated alcohols and carboxylic acids; the carboxyl group tends to produce the nickel salt and hydrogen, although at 180° the equilibrium is moving in the direction of reduction, whilst with the alcohol there is a tendency toward dehydration. On the other hand, unsaturated aldehydes and ketones show a normal reduction with increase in the hydrogen concentration. In general, an increase of the hydrogen concentration causes a directly proportionate increase in the rate of hydrogenation, provided that there are no disturbing factors; the increase of hydrogenation becomes abnormally large if other groups active toward nickel, but not open to hydrogenation, are also present. The nature of the unsaturated organic compound has a determining influence on the effect of the hydrogen concentration.

J. F. S.

**Catalysis of the Mutarotation of Dextrose by Metals.** WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN (T., 1921, **119**, 1936—1948).

**Oxidation Catalysis. I.** L. KARCZAG (*Biochem. Z.*, 1921, **117**, 69—86).—A group of colouring matters was subjected to the action of hydrogen peroxide under various experimental conditions in the presence of iron, copper, cobalt, manganese, nickel, and platinum salts. The conclusion is drawn that the first four metals named have a two-fold action, like that of catalase and oxydase respectively, whilst the two latter have only an oxydase-like action.

H. K.

**Magnitude of Atoms.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1921, **43**, 1584—1591).—A theoretical paper in which it is pointed out that the contraction suffered during combination, taken in connexion with the compressibilities of the elements combined, makes possible an approximate estimate of the bulk occupied by the several constituents in a compound. Calculations are made of the diameters of the atoms of the halogens and the alkali metals in the alkali haloids when the following values in Ångström units are obtained: (*a*) in chlorides, chlorine, 2·8; lithium, 2·3; sodium, 2·9; potassium, 3·5; rubidium, 3·8; cæsium, 3·8; (*b*) in bromides, bromine, 3·1; lithium, 2·4; sodium, 2·9; potassium, 3·5; rubidium, 3·8; cæsium, 3·7; (*c*) in iodides, iodine, 3·4; lithium, 2·6; sodium, 3·1; potassium, 3·7; rubidium, 3·9; cæsium, 3·8. These values lie about half-way between the values obtained by Bragg and Landé. Emphasis is placed on the importance of considering the compressing effect of the affinities concerned in

making any comparison of atomic volume. A series of volumes of the individual halogen and alkali metal atoms in alkali haloids is given in the paper. J. F. S.

**Analysis of the Atomic Structure.** A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 1077—1079; cf. A., 1921, ii, 669).—A table is given showing the number of internal electrons and the number of quanta for each layer in the heavy atoms, and these data are discussed. A periodic table is given illustrating the author's theory of electronic structure of the elements, and from it, it is shown that the chemical analogy of the different elements depends, not only on the number of superficial corpuscles, but also on the sub-jacent electronic layer. The table enables the transformations that will be observed in the $X$-spectrum of the light elements to be foretold. W. G.

**Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules.** CHARLES R. BURY (*J. Amer. Chem. Soc.*, 1921, **43**, 1602—1609).—A theoretical paper in which an alternative has been suggested to the fourth postulate in Langmuir's arrangement of electrons in atoms and molecules (A., 1919, ii, 328). This avoids the necessity of postulating cells in the structure of the atom, and leads to different structures for the elements of higher atomic weights than that of neon. It is claimed that the application of Lewis and Langmuir's octet hypothesis of valency to these structures gives a better explanation of the chemical properties of the higher elements than can be obtained from Langmuir's structures. J. F. S.

**Motion of Electrons in Gases.** J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1921, [vi], **42**, 873—891).—An account is given of the method of finding the velocities of electrons in gases, and the application of the results to determine some properties of gaseous molecules. The paper also contains the results of a large number of experiments which have been made on the motion of electrons in hydrogen, nitrogen, and oxygen with ranges of forces and pressures similar to those used in experiments with air. J. F. S.

**New Type of Sodium Lamp for Polarimetry.** HAROLD A. FALES and JACQUES C. MORRELL (*J. Amer. Chem. Soc.*, 1921, **43**, 1629—1630).—A sodium lamp for use in all cases where a continuous sodium flame is required is described. The lamp consists of a small alundum thimble supported by nickel or nichrome wire in the flame of a Méker burner. The molten sodium chloride contained in the thimble slowly percolates through the pores of the thimble, so that the flame is continuously fed by sodium chloride vapour. J. F. S.

**Rotary Burner with Fixed Gas Connexion.** GEORG LOCKEMANN (*Z. angew. Chem.*, 1921, **34**, 594—595).—A modification of the rotary burner previously described (A., 1921, ii, 447) enables an ordinary Teclu burner with a non-flexible gas connexion to be

used. The burner tube is fitted into the hub of the horizontal pulley, and is continued on the upper side by a tube bent four times at right angles and jointed in the central vertical limb, so that the upper portion can be twisted round to bring the gas outlet to any desired distance from the axis of rotation of the pulley. A fitting is also provided to fix on the top of the burner tube to give an oblique instead of a vertical flame. G. F. M.

## Inorganic Chemistry.

**Molecular Volumes, Physical Properties, and Molecular Models of the Halogens.** F. A. HENGLEIN (*Z. anorg. Chem.*, 1921, **118**, 165—171).—It has been shown by Biltz (A., 1921, ii, 437, 487) that there is a linear relation between the molecular volumes of the halogens and of their compounds. It is now shown that there is likewise a linear relation between the atomic volumes of the halogens at their boiling points and others of their physical properties including melting point, boiling point, critical point, latent heat of fusion or of evaporation, and normal potential; also between the molecular volumes of the halogen acids at the boiling point and many other of their physical constants. Owing to the close similarity in structure of the different halogen atoms, their properties are determined principally by the atomic radius. In contrast with most groups of the periodic system, the molecule of a halogen element has an especially simple structure; it can be represented diagrammatically by two cubes having a common edge, with the valence electrons situated at the corners.

E. H. R.

**The Catalytic Formation of Hydrogen Chloride from Hydrogen and Chlorine without Explosion.** BERNHARD NEUMANN [with BERGDAHL, BROY, and KARWAT] (*Z. angew. Chem.*, 1921, **34**, 613—620).—All non-explosion methods for the synthesis of hydrogen chloride gas yield a product contaminated with chlorine. Hoppe, who first suggested the use of metallic chlorides as catalysts to this reaction employed the chlorides of aluminium, tin, and zinc in concentrated solution at a temperature of 130°. A repetition of his work has shown that, under the most favourable conditions and with a very slow current of gas not more than 70% conversion is obtained. The reaction is favoured by an increase of concentration and of temperature, but a practical limit is set to the latter by the point at which evaporation becomes rapid. The author has used solid chlorides and higher temperatures. The hydrogen and chlorine were generated electrolytically in separate cells in the same electric circuit, passing into a mixing flask containing water and thence to a quartz tube in the shape of a pipette filled

with granules of quartz impregnated with the selected chloride and heated. The emerging gases were absorbed in a 10-bulb potash tube. The mixed gases were shielded from light and drawn through the apparatus by uniform slight suction, fluctuation of pressure being a source of explosions. With a low gas velocity, a complete conversion was effected by magnesium chloride at 300°, by calcium chloride at 305°, by aluminium chloride (which at this temperature is almost entirely decomposed) at 350°, and by quartz unimpregnated by any salt at 380°. Conversion was improved by warming the mixing flask to 50°, with the effect of adding 1 mol. of water to each mol. of hydrogen chloride, this temperature being an optimum. The dilution of the gases with oxygen had at 380° no influence on the reaction. The reactions $Cl_2+H_2O=ClOH+HCl$, $ClOH+H_2=H_2O+HCl$ are considered to occur, removal of the hydrogen chloride generated being facilitated by the partly dissociated chlorides. C. I.

**Sulphate-free Sulphites for Standard Sulphur Dioxide Solutions.** S. Lantz Shenefield, Frank C. Vilbrandt, and James R. Withrow (*Chem. and Met. Eng.*, 1921, **25**, 953—955).—Pure sodium sulphite heptahydrate was prepared by passing carefully purified sulphur dioxide into a solution of sodium carbonate to saturation, adding the requisite amount of sodium carbonate to transform the resultant sodium hydrogen sulphite into the normal sulphite, and cooling the solution to 0°, whereby a crystalline meal of the heptahydrate was obtained. All the operations were carried out in the absence of oxygen and the damp crystals were found to be free from sulphate. They were placed in a desiccator over sulphuric acid and sodium pyrogallate was used as oxygen absorbent. Although every precaution was taken to exclude air leakage, the crystals after one week contained 7·52% of sodium sulphate decahydrate. Similar oxidation occurred in the preparation of pure dry calcium sulphite, and the opinion is expressed that in both cases this is due to autoxidation of the salt. It is concluded that the validity of all investigations in the literature based on the preparation of sulphate-free sulphite for use as a sulphur dioxide standard is doubtful. A. R. P.

**Polythionic Acids and Polythionates.** E. H. Riesenfeld and G. W. Feld (*Z. anorg. Chem.*, 1921, **119**, 225—270).—A method has been devised for estimating the proportions of tri-, tetra-, and penta-thionates together in solution with sulphite, thiosulphate, and sulphate, and the method has been applied to the study of the formation and stability of the polythionates. The hexathionic acid described by Debus (T., 1888, **53**, 278) does not exist. The total polythionic acids can be determined by treatment in neutral solution with a mercuric salt, when four equivalents of sulphuric acid are produced for each molecule of polythionate, for instance: $2S_5O_6''+2Hg^{\cdot\cdot}+4H_2O=2HgS+4SO_4''+8H^{\cdot}+4S$. The acid can then be titrated. Alternatively, the polythionates can be oxidised with bromine in alkaline solution; the whole of the sulphur is oxidised to sulphate and is precipitated and weighed

as barium sulphate. The trithionate is estimated by boiling the solution with an excess of copper sulphate, when the following reaction occurs: $S_3O_6'' + Cu^{••} + 2H_2O = CuS + 2SO_4'' + 4H^{•}$. The copper sulphide is filtered, ignited, and weighed as copper oxide. When boiled with excess of alkali, the polythionates form thiosulphate and sulphite thus: $2S_3O_6'' + 6OH' = S_2O_3'' + 4SO_3'' + 3H_2O$; $2S_4O_6'' + 6OH' = 3S_2O_3'' + 2SO_3'' + 3H_2O$; $2S_5O_6 + 6OH' = 5S_2O_3'' + 3H_2O$. The sulphite and thiosulphate formed are estimated by titration with iodine. By applying three of these reactions, data can be obtained from which to calculate the proportions of tri-, tetra-, and penta-thionate present.

The interaction between hydrogen sulphide and sulphur dioxide was studied by leading a current of the former, as gas, into an aqueous solution of the latter at 0°, until a definite ratio of the reacting substances was present in solution. The total polythionate was estimated after sixty hours. The optimum ratio for polythionate formation was $2SO_2 : 1H_2S$. On the other hand, with the ratio $2H_2S : SO_2$, all the sulphur was precipitated in the elementary form. Evidence was obtained that, immediately after the preparation of a solution in the ratio $2SO_2 : H_2S$, an intermediate compound is formed which can be precipitated at a low temperature as the barium salt; in solution, this changes to barium thiosulphate. The proportion of tri- and tetra-thionic acids formed (determined after fourteen days) depends on the sulphur dioxide concentration, the formation of tetrathionic acid being favoured by low concentration. The proportion of pentathionic acid is, however, practically constant. These results are contrary to those obtained by Heinze (A., 1919, ii, 334). The sulphuric acid which is always formed reaches a maximum near the commencement of the reaction; it must therefore be formed from the intermediate compound, not by oxidation of the polythionic acids.

Of the three polythionic acids, the tetrathionic acid is the least stable and decomposes relatively quickly into tri- and pentathionic acids. The trithionic acid decomposes more slowly with formation of sulphur dioxide, whilst pentathionic acid decomposes only in the course of months with separation of sulphur. The order of stability is the same in neutral as in acid solution; in alkaline solution all the polythionates decompose qnickly into thiosulphate and sulphite.

The phenomena observed are explained on the assumption that the above intermediate compound is a hydrate of the unknown sulphur monoxide, SO. This is stable in acid solution for a time, but in neutral or alkaline solution quickly forms thiosulphate. In acid solution, it slowly polymerises to pentathionic acid. By combination with sulphurous acid it forms tri- and tetra-thionic acid: $3SO + H_2SO_3 = H_2S_4O_6$; $SO + 2SO_2 + H_2O = H_2S_3O_6$. By hydrogen sulphide, it is reduced to sulphur. E. H. R.

**The Preparation of Hydrogen Selenide from Metallic Selenides.** L. Moser and E. Doctor (*Z. anorg. Chem.*, 1921, **118**, 284—292).—The selenides of magnesium, aluminium, iron,

and zinc were prepared in a similar manner to the corresponding tellurides (this vol., ii, 48) by passing selenium vapour over the heated metal in a vacuum. The aluminium and magnesium compounds were also prepared by direct combination of the metal with selenium in a crucible, starting the reaction between the mixed components with a burning magnesium wire. All the products were considerably contaminated with metal except aluminium selenide, which, prepared by the latter process, was practically pure. *Aluminium selenide*, $Al_2Se_3$, forms a light brown powder, unstable in air, and *magnesium selenide*, MgSe, is very similar. *Zinc selenide*, ZnSe, is citron-yellow and *iron selenide*, FeSe, is black and metallic; both are stable in air.

Hydrogen selenide was prepared in an apparatus similar to that used for hydrogen telluride, by dropping the metallic selenide slowly into acid. The best results were obtained using aluminium or magnesium selenide. The gas was liquefied at the temperature of a solid carbon dioxide–ether mixture and by revaporisation was obtained pure. It is not decomposed by daylight in the liquid or gaseous form, but is sensitive to ultra-violet light. Dry oxygen has no action on the dry gas, but in presence of moisture decomposition is rapid. E. H. R.

**Selenious Acid and Heteropolyselenites.** ARTHUR ROSENHEIM and LEONHARD KRAUSE (*Z. anorg. Chem.*, 1921, **118**, 177—192).—A large number of heteropolyselenites with vanadates and molybdates have been described by Prandtl and others (A., 1907, ii, 477; 1912, ii, 167; 1916, ii, 333), who described numerous well-crystallised salts which, however, had variable compositions according to the conditions of preparation. These compounds have been re-examined with a view to determine whether they may not have a semi-colloidal constitution similar to that of the periodates (A., 1919, ii, 508). Experiments were first made to determine the state of aggregation of selenious acid in aqueous solution. Depression of the freezing point of water indicated slight association, which has a tendency to decrease with time. The dissociation was determined by the hydrogen-ion concentration method and from the electrical conductivity, the results obtained being $4{\cdot}85 \,.\, 10^{-3}$ and $3{\cdot}45 \,.\, 10^{-3}$ respectively. These results are taken to be consistent with the presence of associated $(H_2SeO_3)_2$ molecules in solution.

The method of estimating selenious acid by heating with potassium iodide and hydrochloric acid and distilling the iodine over into potassium iodide was improved by the addition of phosphoric acid to the hydrochloric acid. This prevents the formation of selenium iodide, which may be the cause of low results. It was also found that selenious acid may be accurately titrated with sodium hydroxide; the best indicators are, for the formation of $NaHSeO_3$, *p*-nitrophenol, and for complete neutralisation to $Na_2SeO_3$, thymolphthalein.

*Lithium selenite* forms the hydrate $4Li_2SeO_4,3H_2O$; its solubility has a negative temperature coefficient.

*Molybdoselenites.*—The composition of molybdoselenites was found to depend on the ratio of molybdate to selenious acid in the solution from which they were precipitated. When less than 1 mol. of selenium dioxide was present to 1 mol. of molybdate, the potassium and barium salts corresponded with $2R_2O,2SeO_2,5MoO_3xH_2O$ and the ammonium salt with $3(NH_4)_2O,2SeO_2,8MoO_3,6H_2O$. With more than 1 mol. of selenium dioxide per mol. of molybdate in solution, salts were obtained in which the proportion of base was variable, but the ratio $SeO_2 : MoO_3$ was always very nearly 1 : 1. The *ammonium* salt, $2(NH_4)_2O,5SeO_2,5MoO_3,8H_2O$, white, microscopic prisms, was obtained by adding 15 mols. of selenium dioxide to a saturated solution of ammonium paramolybdate. The *potassium* salt,

$$K_2O,2SeO_2,2MoO_3,3{\cdot}5H_2O,$$

forms microscopic prisms, and the *barium* salt,

$$BaO,2SeO_2,2MoO_3,7H_2O,$$

a white, crystalline precipitate.

*Vanadioselenites.*—Vanadioselenious acid has the composition $4SeO_2,3V_2O_5,10H_2O$. An extensive series of experiments showed that, as the concentration of selenious acid in the mother-liquor increased from zero to $5N$, the ratio of $SeO_2$ to $V_2O_5$ in the solid phase increased from 4 : 3 to 5·5 : 3. Similar behaviour was shown by the ammonium vanadioselenites having the approximate formula $3(NH_4)_2O,12SeO_2,8V_2O_5$. It is concluded that the variable composition of the vanadic acid compounds is due to the formation of adsorption compounds, although in the case of the molybdic acid compounds this is not no clearly demonstrated. E. H. R.

**The Preparation of Hydrogen Telluride from Metal Tellurides.** L. Moser and K. Ertl (*Z. anorg. Chem.*, 1921, **118**, 269—283).—A new method for preparing metal tellurides was devised which consisted in distilling tellurium at a low pressure (8 mm.) over the hot, finely divided metal. In this way the tellurides of magnesium, MgTe, aluminium, $Al_2Te_3$, iron, FeTe, and zinc, ZnTe, were prepared. The aluminium compound was obtained in an almost pure state; it is a blackish-brown, lustrous, amorphous substance, decomposing in the air with formation of tellurium hydride. The other tellurides were all more or less contaminated with excess of the respective metal. Magnesium telluride forms a brown, sintered mass, iron telluride is grey and metallic, and zinc telluride is pale hrown. The last two are stable in air. For the preparation of hydrogen telluride a special apparatus was designed, in which the powdered metallic telluride was dropped very gradually into acid in an atmosphere of nitrogen. Aluminium telluride proved the most suitable substance from which to generate the gas, and hydrochloric acid the best acid to use. The yield of gas obtained under the best conditions was more than 80% of the theoretical. The gas was liquefied by passing through a tube immersed in a mixture of solid carbon dioxide and ether. In the liquid state hydrogen telluride is very sensitive both to daylight and violet light, hut the dry gas is quite stable in light. The dry Thowever, immediately oxidised by oxygen. E. H. R.

Selenı

**The Preparation of Telluric Acid.** JULIUS MEYER and HANNS MOLDENHAUER (*Z. anorg. Chem.*, 1921, **119**, 132—134).—Telluric acid can be prepared in a pure state and in almost theoretical yield by oxidation of tellurium tetrachloride with chloric acid. Tellurium (10 grams) is boiled with 10 c.c. of nitric acid and 3 c.c. of hydrochloric acid until completely dissolved. To the hot solution is added gradually a concentrated solution of 9 grams of chloric acid and the solution is boiled until no more chlorine is evolved. A slight excess of chloric acid is added to avoid formation of any explosible chlorine oxide. The solution is filtered through asbestos and concentrated by distillation in a vacuum on the water-bath, thereby removing chlorine. The telluric acid can be crystallised out by the addition of concentrated nitric acid, collected, and finally freed from chlorine and nitrogen oxides by drying in a vacuum. It is obtained as a crystalline, snow-white powder, readily soluble in water, having the composition $H_6TeO_6$. E. H. R.

**Vapour Pressures of Ammonia-Salt Solutions.** R. O. E. DAVIS, L. B. OLMSTEAD, and F. O. LUNDSTRUM (*J. Amer. Chem. Soc.*, 1921, **43**, 1580—1583; cf. this vol., ii, 56).—Vapour pressure curves have been constructed for the following solutions: $Ca(NO_3)_2$ 22·48%, $NH_3$ 19·18%, $H_2O$ 58·34%; NaI 32·34%, $NH_3$ 6·06%, $H_2O$ 51·60%; $NH_4$·CNS 77·84%, $NH_3$ 22·16%; $NH_4NO_3$ 33·7%, $NH_3$ 18·82%, $H_2O$ 47·48%; $CaCl_2$ 12·9%, $NH_3$ 22·9%, $H_2O$ 64·2%; $Ca(NO_3)_2$ 55·8%, $NH_3$ 25·77%, $H_2O$ 18·43%; $NH_3$ 28·15%, $H_2O$ 71·85%; NaI 64·88%, $NH_3$ 26·02%, $H_2O$ 9·20% over the temperature range −16° to 40°. It is shown that solutions of ammonium nitrate in ammonia and ammonium thiocyanate are very corrosive to iron and steel, the calcium chloride–ammonia solution is less corrosive, and calcium nitrate–ammonia, and sodium iodide–ammonia solutions show no immediate corrosive action. Calcium nitrate–ammonia solutions seem to be the most promising of these solutions for practical use as an absorbent for ammonia in the synthetic ammonia process. J. F. S.

**The Action of Metals, such as Copper and Zinc, on an Aqueous Solution of Ammonium Nitrite.** N. R. DHAR (*Z. anorg. Chem.*, 1921, **119**, 174—176).—The action of a solution containing ammonium nitrite on copper was attributed by Hofmann and Buhk (A., 1921, ii, 43) to the hydrolysis of the nitrite with formation of free nitrous acid. The observation that the metal is attacked even in presence of urea, however, renders this explanation improbable. Further, solutions of other nitrites such as zinc nitrite, which are hydrolysed as much as ammonium nitrite, do not attack copper. The activity of the ammonium nitrite is probably related to its instability and ready decomposition into nitrous oxide and water. E. H. R.

**The Structure of Pyrophosphoric Acid. III.** D. BALAREFF (*Z. anorg. Chem.*, 1921, **118**, 123—130; cf. A., 1915, ii, 446; 1917, ii, 467).—In previous papers it has been shown that there is a good

deal of evidence in favour of the unsymmetrical structure of pyrophosphoric acid. The synthesis of the pyro-acid by combination of the ortho- and meta-acids in sulphuric acid would give added support to the hypothesis of an unsymmetrical structure, but attempts in this direction were not successful, even in acid containing 15% of free sulphuric anhydride.

The change of colour of the salt $NaAg_3P_2O_7$ from white to yellow on heating has been attributed to its decomposition into $NaPO_3$ and $Ag_3PO_4$, but it is now shown that this does not occur, the colour change being probably due to some physical change in the salt.

No evidence as to the structure of the pyro-acid could be gained from a study of the dehydration of dihydrogen phosphates of alkali metals. The potassium salt heated at 244° loses water and changes to the acid pyrophosphate, $K_2H_2P_2O_7$; the rubidium salt behaves in the same way. The sodium salt loses water very slowly at 180° and in the course of about one hundred and seventy-eight hours becomes completely converted into $Na_2H_2P_2O_7$. The products of further dehydration at a higher temperature depend on the water vapour pressure. In moist air at 305°, only soluble metaphosphate is formed, whilst in dry air at 330° about 75% of the metaphosphate formed is insoluble.

Phosphoryl bromide dehydrates orthophosphoric acid to pyrophosphoric acid, but not to the meta-acid. The action is a complex one, and depends on the temperature and proportions of the interacting substances.

A dilute solution of an alkali pyrophosphate, after prolonged boiling, shows the presence of orthophosphate, proving that hydration occurs slowly. E. H. R.

**Iso- and Heteropoly-acids. XVII. Polyborates in Aqueous Solution.** ARTHUR ROSENHEIM and FELIX LEYSER (*Z. anorg. Chem.*, 1921, **119**, 1—38).—An attempt was made to prepare simple and complex polyborates with the object of comparing these with salts of other acids such as telluric, antimonic, periodic, plumbic, and stannic acids, which show semi-colloidal properties. Methods for the quantitative estimation of boric acid were examined. The polarimetric method, depending on the influence of boric acid on the optical rotation of tartaric acid, is of limited application on account of the disturbing influence of salts or other substances present in solution. Titration with sodium hydroxide in presence of mannitol, using phenolphthalein as indicator, gives trustworthy results. *Free boric acid in the presence of borate can be detected* by boiling a sample of the substance for some minutes with dry acetone, filtering, evaporating the filtrate on a watch glass, moistening with a few drops of methyl alcohol, and igniting, when the *characteristic flame coloration is given if free boric acid is present.*

An investigation of the equilibrium in the system $Na_2O$–$B_2O_3$–$H_2O$ at 0° confirmed the existence of the three salts, $Na_2O,B_2O_3,8H_2O$, $Na_2O,2B_2O_3,10H_2O$, and $Na_2O,5B_2O_3,10H_2O$. Sodium pentaborate can readily be crystallised from solutions containing $Na_2O$

and $B_2O_3$ in the ratio 1 : 5, but sometimes only crystals of borax are obtained, probably because the pentaborate is metastable at ordinary temperatures and borax is the less soluble salt. Potassium pentaborate, $K_2O,5B_2O_3,8H_2O$, is a well-defined, characteristic salt, separating from solutions in which the ratio $B_2O_3$ : KOH is 3 : 1 or higher. Its solubility is very low, not much greater than that of potassium perchlorate. Potassium monoborate crystallises with $8H_2O$ at 0°, with $2{\cdot}5H_2O$ at 30°. Rubidium pentaborate is very similar to the potassium salt, but crystallises with $10H_2O$. Thallium pentaborate, like the potassium salt, crystallises with $8H_2O$, but is more soluble than the latter. Guanidine forms a diborate crystallising iu elongated prisms with $4H_2O$ and a pentaborate with $8H_2O$.

Experiments on the dehydration of pentaborates showed that, in the general formula $R_2O,5B_2O_3,xH_2O$, two molecules of water are probably constitutively combined. Conductivity experiments indicated that in dilute aqueous solution the pentaborate anion is hydrolysed into the diborate anion and boric acid. In presence of great excess of boric acid this hydrolysis is prevented, and the specific conductivity of sodium pentaborate at 0° appears to be 85% of that of sodium diborate. Experiments on the hydrogen-ion concentration of solutions containing varying ratios of NaOH to $B_2O_3$ confirm the existence of a pentaborate ion in concentrated solution.

The pentaborate ion appears to form complex anions with a number of metals. Whilst borax solution immediately precipitates zinc or cadmium hydroxide from a solution of a salt of the metal, sodium pentaborate does not. Cobaltous hydroxide dissolves in sodium pentaborate solution to form a red solution in which, although alkalis do not readily precipitate it, the cobalt is in the kation. When this solution is oxidised with bydrogen peroxide, however, some cobaltic oxide is precipitated and a yellow solution is formed containing a complex cobalt anion. Nickel, chromium ($Cr'''$), manganese ($Mn''$), and copper also appear to form complex anions. A very small quantity of a copper compound was isolated, having approximately the composition $2Na_2O,4CuO,12B_2O_3,50H_2O$.

E. H. R.

**The Atomic Weight of Carbon.** E. MOLES (*Anal. Fis. Quim.*, 1921, **19**, 255—259).—The value 12·005 for the atomic weight of carbon given by Richards and Hoover (A., 1915, ii, 96) is held to be based on an erroneous value for the atomic weight of sodium. The value 12·000 is claimed to be more exact. G. W. R.

**The Oxidising Properties of Carbon Suspensions.** F. FEIGL (*Z. anorg. Chem.*, 1921, **119**, 305—309).—The oxidising effect of blood charcoal was studied in a qualitative manner by boiling solutions of different oxidisable substances with a suspension of the charcoal. In acid solution, hydrogen sulphide was oxidised to sulphuric acid, potassium iodide to iodine, mercurous salts to mercuric, oxalic acid to carbon dioxide. In alkaline solu-

tion, potassium iodide was oxidised to iodate, alkaline sulphides and sulphites to sulphate, cuprous and cupric sulphides to copper sulphate, cobalt sulphide to sulphate, potassium chromite to chromate. Sodium thiosulphate was unacted on in alkaline or neutral solution, and sodium nitrite was unaffected in alkaline solution. A quantitative study of the oxidation of tervalent chromium to chromate was made, after a method had been devised for removing from the solution a product, formed by the interaction of the charcoal and potassium hydroxide, which liberates iodine from potassium iodide. This was accomplished by boiling with potassium permanganate and removing the excess with hydrogen peroxide. The experiments showed that the proportion of chromate formed increased with the proportion of charcoal used, but that, with a constant quantity of charcoal, the amount of chromate formed increased with the quantity of chromium salt taken. Different charcoals varied widely in their oxidising power, but the differences seemed to bear no relation to the ash content.

E. H. R.

**Aqueous Carbonic Acid Solutions.** E. WILKE (*Z. anorg. Chem.*, 1921, **119**, 365—379).—The dissociation constant of carbon dioxide solutions was measured by the conductivity method, using a solution through which the gas was being continuously circulated. When an ordinary saturated solution was used, without circulation, the conductivity was found to increase during measurement, probably through electrolytic changes caused by the current. Even with the greatest precautions, variable results were obtained, confirming the observations of earlier workers. It was observed that, by contact with the metal electrodes (gold), even without passage of current, the conductivity gradually increased. In three hours the dissociation constant $K.10^7$ increased from 3·07 to 4·5. Light seemed to have an effect in the same direction. For measuring the hydrogen-ion concentration, a special hydrogen electrode was used consisting of a palladium capillary into which hydrogen was forced at a pressure of 20 atm. The hydrogen-ion concentration was determined in presence of sodium, potassium, and barium chloride. In these solutions carbon dioxide has the character of a strong acid, increasing with the concentration of salt. The hydrogen-ion concentration increases more rapidly than the total carbon dioxide concentration. The observations can be explained on the assumption that a solution of carbon dioxide in water contains orthocarbonic acid, $H_4CO_4$, which, containing no ketonic oxygen, is a very weak acid. In concentrated salt solutions it is dehydrated to form the strong acid $CO(OH)_2$. E. H. R.

**Behaviour of Amorphous Carbon and Sulphur at High Temperatures. Carbon Sulphides.** J. P. WIBAUT (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92—101).—The action of sulphur on amorphous carbon at high temperatures has been investigated. Pure sugar charcoal has been heated with sulphur at temperatures from 400° to 1000° under reduced pressure for

prolonged periods of time. A slow evolution of hydrogen sulphide, due to the small amount of hydrogen present in the carbon, is observed and a carbon-like substance containing 1·98% of sulphur obtained. This substance yields no sulphur to toluene, even after prolonged boiling, and the residue after this treatment contained 2·03% of sulphur. Prolonged heating in a vacuum at temperatures up to 1010° did not reduce the sulphur content nor was any volatile compound obtained. Prolonged shaking with bromine water oxidised 9% of the sulphur to sulphuric acid, and heating in a current of hydrogen at temperatures up to 750° removes 77% of the sulphur as hydrogen sulphide; this reaction is exceedingly slow and must be regarded as an action between a sulphur compound and hydrogen and not as an action between hydrogen and sulphur vapour. This was further proved by the fact that heating in nitrogen did not reduce the sulphur content. The author considers that a solid carbon sulphide is formed which bears a strong resemblance to coal coke (cf. Stock and Praetorius, A., 1913, ii, 46). A further sulphide containing 3·5% of sulphur has been obtained by heating carbon purified by chlorine with sulphur. This substance has similar properties to the compound containing 2·0% of sulphur. J. F. S.

**The Deviations from the Gas Laws of Carbon Disulphide.** ALFRED SCHULZE (*Z. anorg. Chem.*, 1921, **118**, 223—230).—A number of observations on the properties of carbon disulphide vapour indicate that it is associated to a small extent. The increase of pressure observed when carbon disulphide and ether vapours are mixed at constant volume at 80° under atmospheric pressure indicates association of the former to the extent of 0·14%, whilst vapour density determinations by Dumas's method give results corresponding with 2% association. Compressibility experiments at 80° showed 0·5% more association at 2 atmospheres than at 1 atmosphere pressure. The *PV* curves at 78·82° and 130·48° show that the amount of association decreases with increasing temperature, but at constant temperature increases with increasing pressure. It is probable that in the liquid phase association is more considerable. E. H. R.

**New Theory of the Constitution of Hydroxides, particularly those of the Basic Metallic Oxides.** FR. TIEMANN (*Chem. Zeit.*, 1921, **45**, 1125).—To furnish an explanation for a number of phenomena in organic, inorganic, and electrolytic processes which are not in consonance with existing ideas, the author proposes a new theory of the constitution of the hydroxides of the pronounced electropositive metals. It is suggested that these compounds do not contain hydroxyl groups, but are to be regarded merely as true hydrates of the corresponding oxides, that is to say that sodium and calcium hydroxides, for example, are not correctly represented by the formulæ NaOH and $Ca(OH)_2$ but are actually $Na_2O,H_2O$, and $CaO,H_2O$, a molecule of water being closely associated with the metallic oxide similarly to the "water of

crystallisation" of salts. This applies to all the elements of groups I and II of the periodic system, whilst the constitution of the hydroxides of those of groups III and IV (aluminium, zinc) will depend on the electrochemical conditions under which they are produced. Only the hydroxides of the metalloids and non-metals are to be regarded invariably as true hydroxyl derivatives. With increasing basicity of the oxides the associated water molecules become increasingly firmly bound exactly as in the case of the increasingly basic character of salts containing associated water. So the dehydration of the hydroxides of calcium, strontium, and barium is effected with increasing difficulty in the order named.

The sucrosates are cited to illustrate the application of the theory. If calcium hydroxide is regarded as a hydroxyl compound, the chemical character of sucrose or dextrose is quite incompatible with the idea of a "neutralisation" of hydroxide, looked on as a generator of hydroxyl ions. There can therefore only be a question of the displacement of the associated water by the sugar, and the sucrosates must be formulated $C_{12}H_{22}O_{11},2CaO$, $C_6H_{12}O_6,CaO$, etc. The isomerism of the hydroxides of tin and aluminium is also explained by reference to the theory, *e.g.* $Al(OH)_3$ and $Al_2O_3,H_2O+2H_2O$ can both exist as individual substances, and either one or the other will be produced according to the conditions of the reaction. The non-appearance of hydrogen peroxide, derived from the union of two hydroxyl groups, during electrolysis of a metallic hydroxide is explained by the new theory as due to the absence of hydroxyl groups. The electrolysis actually is that of, say, $Na_2O,H_2O$, the associated water taking no part in the process. There takes place simply a direct fission into metal and oxygen which are liberated at their respective poles. An assumption of the appearance of hydroxyl ions in any electrolytic process is quite unjustified. G. F. M.

**Preparation of Alcoholic Potassium Hydroxide Volumetric Solution.** S. T. McCallum (*J. Ind. Eng. Chem.*, 1921, **13**, 943).—A solution which does not darken in colour when kept is prepared by dissolving potassium hydroxide in methyl alcohol (purified wood spirit); the solution must be filtered through glass-wool to remove insoluble potassium carbonate, etc., before it is used. W. P. S.

**Existence of Tetra-hydrated Sodium Sulphate in Mixed Crystals with Sodium Chromate.** Theodore W. Richards and W. Buell Meldrum (*J. Amer. Chem. Soc.*, 1921, **43**, 1543—1545).—It is shown that crystals of the tetrahydrate of sodium chromate, $Na_2CrO_4,4H_2O$, dissolve sodium sulphate as $Na_2SO_4,4H_2O$, a form of sodium sulphate otherwise unknown, to the extent of somewhat less than half the quantity corresponding with the same weight of sodium chromate in the supernatant liquid. When sodium sulphate was in large excess, no crystallisation could be induced by "seeding" the saturated mixture with the crystals of the mixed tetrahydrate above the transition temperature of sodium

sulphate, and below this temperature only crystals of the decahydrate could be formed. Thus under these conditions the tetrahydrate is so much more soluble than the phases containing more sodium sulphate as to be incapable even of metastable existence.

J. F. S.

**Ammonium Radicles. III. Ammonium.** Hans Heinrich Schlubach and Fritz Ballauf (*Ber.*, 1921, **54**, [*B*], 2825—2834; cf. A., 1920, i, 822 and this vol., i, 15).—The authors' experience with tetraethylammonium leads them to expect that the ammonium radicle would be extremely sensitive to rise in temperature and that there is no hope of isolating it by the electrolyses of solutions of ammonium salts in liquid ammonia on account of the impossibility of avoiding the thermal effect of the current, and that the only prospect of success lies in displacement reactions effected at a low temperature. They find that when well-cooled ammonium chloride is added to a solution of potassium in liquid ammonia at −70° in the apparatus described previously for the preparation of tetraethylammonium, decolorisation of the solution takes place before the calculated volume of hydrogen has been evolved, the deficit amounting to as much as 65%; according to Moissan, the whole of the hydrogen is evolved by the time the solution becomes colourless. The deficit cannot be attributed to the solubility of hydrogen in liquid ammonia since this is shown to be too small to account for the observed effect, and it appears therefore that colourless ammonium is actually present in the solution. This conclusion is supported by the observation that the remainder of the hydrogen is evolved rapidly when the solution is cautiously warmed at about −40°. Repetition of Moissan's experiment shows that the non-observation of the production of ammonium is due to operation in too concentrated solution and consequent decomposition of the radicle by the heat liberated during the reaction. When a solution of potassium (1·8%) is added to a solution of ammonium chloride (1%) in liquid ammonia at −70°, a violent reaction is observed and each drop of added solution is immediately decolorised, formation of ammonium and its conversion into the colourless form appearing to occur instantaneously; tetraethylammonium and ammonium, therefore, stand to one another in the same relationship as triphenylmethyl to methyl. In spite of the violence of the reaction, the yields of ammonium by this method are good and readily reach 50%; the influence of concentration is, however, again apparent, and it is to be expected that an improvement in yield would be observed with more dilute solutions.

The behaviour of ammonium towards the reagents used with tetraethylammonium is described. Corresponding with the rapid isomerisation to the colourless form, the equilibrium is here greatly displaced in the direction of the latter, and it is probable that dissociation and consequent reaction only occur in close proximity to the temperature of decomposition. A reaction with dimethylpyrone could not be observed. Iodine, on the other hand, appears

to react immediately with ammonium, but the quantitative examination of this change could not be completed on account of the experimental difficulties involved. H. W.

**Vapour Pressure of the System, Lithium Nitrate : Ammonia.** R. O. E. Davis, L. B. Olmstead, and F. O. Lundstrum (*J. Amer. Chem. Soc.*, 1921, **43**, 1575—1580).—The solution of ammonia in lithium nitrate has been studied with the object of finding an absorbent for ammonia in the synthetic production of this gas. The use of ammonium nitrate (Kurilov, A., 1898, ii, 156) and ammonium thiocyanate (Foote and Hunter, A., 1920, ii, 246) suffers from the serious drawback that the liquids produced, when these salts adsorb ammonia, attack metals rapidly. A large number of salts have been tested as to their suitability for this purpose, and of these lithium nitrate alone forms a liquid with ammonia in the absence of water, whilst calcium nitrate tetrahydrate liquefies in the presence of a little water. The ammonia contained in 1 c.c. of the lithium nitrate solution saturated at 24° is equivalent to 26·0 c.c. of 0·95*N* sulphuric acid, whilst that for tbe calcium nitrate solution under identical conditions is 18·5 c.c. of 0·95*N* acid. Vapour pressure measurements have been made for the solution 36·34% ammonia, 63·66% lithium nitrate, and for several other mixtures containing 6·06—58·66% of water. The solutions of ammonia in lithium nitrate have no action on machine steel, iron wire, and nichrome wire after several months' contact, but nickel steel shows a slight action after several months. The results show that a solution of lithium nitrate in ammonia with a small percentage of water should be a good absorbent for the removal of ammonia from mixtures of nitrogen, hydrogen, and ammonia. The absorption could be effected at 0° and a large proportion of the ammonia released either by a small increase of temperature or by reduction of the pressure. J. F. S.

**The Reaction between Persulphates and Silver.** Geoffrey Isherwood Higson (T., 1921, **119**, 2048—2055).

**Silver Bromate.** J. H. Reedy (*J. Amer. Chem. Soc.*, 1921, **43**, 1440—1445).—In an earlier paper (A., 1915, ii, 733) it was shown that the electrode $Ag|AgBrO_3|0{\cdot}1NKBrO_3$ only reached a steady value (0·631 volt) after being kept for five days, if the bromate was prepared by the action of bromine on silver nitrate solution, but if it was obtained by double decomposition of silver nitrate and potassium bromate, the correct value was at once obtained. Investigation now shows that silver bromate is dimorphous, existing as tetragonal bi-pyramids and as hair-like crystals. The tetragonal crystals are stable at temperatures below 98·5° (the transition point) and the fine, hair-like crystals are stable above this temperature. Difference of solubility of the two forms explains the irregular behaviour of the electrode mentioned above. The solubility of silver bromate has been determined at temperatures from 25° to 90° and the following values have been found : 25°, 0·196 ; 35°, 0·269 ; 45°, 0·371 ; 55°, 0·497 ; 65°, 0·648 ; 75°, 0·832 ; 85°, 1·055

*and 90°, 1·325, the solubilities being expressed in grams per 100* grams of water. The solubility curve indicates 98·5° as the transition temperature, a value which is confirmed by a dilatometric measurement of this quantity. Dry silver bromate melts at 308—310° and is stable toward heat and light, but in the presence of water it darkens slowly at the ordinary temperature and rapidly at high temperatures. If a little impurity, such as dust, is introduced into heated silver bromate decomposition occurs with explosive violence. Silver bromate crystals absorb a considerable *quantity of air which is slowly evolved at high temperatures.*

It is shown that silver bromate may be used as a standard in iodometry. The method of use consists in placing 1 gram of bromate with an excess of potassium iodide in 150 c.c. of water in a 250 c.c. flask; this is heated on a water-bath to effect double decomposition. The contents of the flask are cooled and made up to 250 c.c. Samples of 25 c.c. are withdrawn, acidified with dilute hydrochloric acid, and titrated with sodium thiosulphate. Arsenious oxide gives a result about 0·2% higher than silver bromate, but after recrystallising the arsenious oxide from hydrochloric acid this figure was reduced to 0·05%. This indicates that whilst silver bromate may have a somewhat higher oxygen equivalent than arsenious oxide, this defect is fully compensated by its greater definiteness. J. F. S.

**Alkali Silver Thiosulphates and their Ability to Add Ammonia.** ERIK JONSSON (*Ber.*, 1921, **54**, [*B*], 2556—2564).—Additive compounds of alkali silver thiosulphate and ammonia have been described previously by Schwicker (A., 1889, 942) and by Meyer and Eggeling (A., 1907, ii, 347), who, however, do not record analyses of their products. A repetition of their work has given somewhat different results. The ability to form additive compounds seems to depend on the presence of unused subsidiary valencies of the silver atom and is most marked in compounds of the type $K_2S_2O_3,Ag_2S_2O_3$; it is scarcely noticeable in the case of the salts $2M_2S_2O_3,Ag_2S_2O_3$ and $5M_2S_2O_3,3Ag_2S_2O_3$. The existence of colourless and yellow alkali silver thiosulphates (cf. Meyer and Eggeling, *loc. cit.*) is confirmed, but it appears doubtful whether their isomerism is explicable by assigning the respective formulæ $AgS{\cdot}SO_2{\cdot}OK$ and $KS{\cdot}SO_2{\cdot}OAg$, since their behaviour towards ethyl iodide indicates that the silver is attached to the sulphur atom in each case. Conversion of the colourless into the yellow modification can be effected frequently by cautious warming with water, but too drastic treatment leads to the formation of silver sulphide, sulphur dioxide, and sulphate. It appears, therefore, that the yellow compounds are intermediate products in the decomposition of the colourless salts, and the transformation is possibly explained by such a scheme as: $KO{\cdot}SO_2{\cdot}SAg \longrightarrow KO{\cdot}S{\cdot}SO_2{\cdot}Ag$.

The following individual substances are described: the *salt*, $2K_2S_2O_3,Ag_2S_2O_3$, colourless prisms, from silver nitrate and potassium thiosulphate in the presence of ammonia; the *salt*, $5K_2S_2O_3,3Ag_2S_2O_3$, long, colourless prisms; the *compound*,

$$3KAgS_2O_3,NH_3,2H_2O$$

(cf. Schwicker, *loc. cit.*, who regards it as $KAgS_2O_3,NH_3$), colourless plates which are converted by warm dilute ammonia and into a yellow *salt* of the same *composition* and are transformed by warm water into the *compound*, $KAgS_2O_3,1{\cdot}5H_2O$, colourless needles, and $KAgS_2O_3$, yellow, hexagonal pyramids; the *salt*, $2NaAgS_2O_3,3H_2O$, small, irregular plates; the *salt*,

$$5(NH_4)_2S_2O_3,3Ag_2S_2O_3,$$

long prisms, and the *compound*, $(NH_4)AgS_2O_3$, prismatic crystals (by the action of ammonium thiosulphate on a solution of silver oxide in ammonia); the *salt*, $5Rb_2S_2O_3,3Ag_2S_2O_3$, colourless prisms (cf. Meyer and Eggeling, *loc. cit.*) which is transformed by warm water into the *salt*, $3Rb_2S_2O_3,4Ag_2S_2O_3$, yellow prisms; the *salt*, $3RbAgS_2O_3,NH_3,2H_2O$ (Meyer and Eggeling record

$$Rb_2S_2O_3,Ag_2S_2O_3,NH_3);$$

the unstable yellow *salt*, $Ag_2S_2O_3,3NH_3,H_2O$. H. W.

**Metallic Hydrides. II. Hydrides of the Alkaline-earth Metals and of Lithium.** FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1921, **4**, 900—924; cf. A., 1921, ii, 638).—The preparation of the hydrides and the measurement of their dissociation tensions is recorded.

When attempts are made to compare the tensions of the different hydrides with one another, it becomes apparent that all measurement of dissociation pressure of the alkali and alkaline-earth hydrides are vitiated by the use of impure material containing a greater or less proportion of dissolved metal which tends to depress the tension. Within each group, the effect of the metal increases with its atomic weight, and the influence of sublimation lies in the same direction. In the cases of cæsium and barium hydrides, these actions render the measurement of dissociation pressures at high temperatures almost impossible. The influence of the atomic weight of the metal on the stability of the alkali hydride cannot be regarded as elucidated completely, but the authors consider from their own experiments that a slight diminution of stability with increasing atomic weight of the metal is probable. The tension curves of lithium hydride could not be measured, since a material which would withstand the chemical action of the hydride and metal could not be found. It is, however, established that it is the most stable of all the alkali or alkaline-earth hydrides which is in accordance with its great heat of formation. Calcium hydride appears to be more stable than barium hydride, whilst the strontium compound occupies an intermediate position.

The behaviour of the alkali and alkaline-earth metals towards hydrogen is not confined to the formation of hydrides, XH and $XH_2$, but extends also to the production of solutions, the phenomenon being more marked with the hydrides of the alkaline earths than with those of the alkalis. The absorption of hydrogen occurs previously to, and, in part, simultaneously with, the formation of the hydrides; this occurs to a greater extent with the alkaline earth than with the alkali metals.

The formation of hydrides occurs slowly with the alkali metals,

rapidly and with incandescence in the cases of the alkaline-earth metals. This appears to be due to the greater solubility of the hydride in the metal. The same explanation applies to the observation that calcium hydride, for example, can be formed at a temperature which is certainly considerably higher than the temperature of dissociation of the pure hydride. The liquid nature of the alkali hydrides at the temperature of their formation contributes also to the slowness of absorption of hydrogen, since the eutectic mass protects the metal from further action.

Investigation of the hydrides of lanthanum and cerium (Muthmann and Baur, A., 1903, ii, 213) and of neodymium and praseodymium (Muthmann and Beck, A., 1904, ii, 409) have given results similar to those now observed with the alkaline-earth metals except that the displacement of the tension due to the presence of an excess of metal is even more considerable. The increase in the action of an excess of metal with increasing atomic weight is therefore apparent not only within a group in the periodic system, but also from left to right with increasing valency of the metal.

H. W.

**The Discovery of an Equilibrium between Cement and Lime-water.** RICHARD LORENZ and GUSTAV HAEGERMANN (*Z. anorg. Chem.*, 1921, **118**, 193—201).—When finely-ground Portland cement, which has been previously treated with water and dried, is stirred with a fixed quantity of water in absence of air, the quantity of lime taken up by the water eventually reaches a maximum value. This maximum is much less than the solubility of lime in water, and depends on the quantity of cement present in proportion to the water, and also, to some extent, on the fineness of the particles. The existence of this maximum is shown to depend on the partition coefficient of lime between the water and the silica–alumina gel formed by the decomposition of the cement constituents such as monocalcium silicate and tricalcium aluminate. This partition coefficient was determined by repeatedly treating the cement with fresh water until the whole of it had decomposed. The ratio of lime in the solid phase to lime in the water was then found to be about 7·0. The existence of the partition coefficient shows that no definite compound is formed between the lime and the constituents of the gel. [See also *J. Soc. Chem. Ind.*, 1922, 15A.]

E. H. R.

**The Solubility of Glucinum Sulphate in Water and Sulphuric Acid at 25°.** HUBERT THOMAS STANLEY BRITTON (T., 1921, **119**, 1967—1971).

**Ammoniates of Magnesium Haloids.** WILHELM BILTZ and GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1921, **119**, 115—131).—For the investigation of the ammoniates of magnesium haloids special precautions were taken in the preparation of pure magnesium chloride, bromide, and iodide. Ephraim's results (A., 1912, ii, 546), which were not confirmed, were probably due to the fact that his magnesium chloride contained basic salts. The

hexammoniate of magnesium chloride is formed in about fifteen hours at room temperature, when pure magnesium chloride is saturated with ammonia, and the product is extraordinarily voluminous. Magnesium bromide behaves similarly, but in the case of the iodide the increase in volume when the hexammoniate is formed is relatively slight. Observations were made on the time taken for the vapour pressure to become steady with different proportions of ammonia in the solid phase. From these observations definite rules can be formulated regarding heterogeneous equilibrium in a solid–gas system. When two non-miscible substances are present in the solid phase, equilibrium is reached with gradually diminishing velocity, usually in the course of a few hours, depending on the temperature and the nature of the substances. When one constituent just disappears, for instance from a mixture containing principally a lower ammoniate and a small quantity of a higher ammoniate, equilibrium is attained very rapidly. When unsaturated mixed crystals are present, for example of two ammoniates, equilibrium is reached very slowly, often requiring several days. This case occurs with the magnesium haloids containing 5·5 to 5·8 mols. of ammonia. When the ammonia content is very nearly 6 mols., addition of a very small quantity of ammonia, even a few hundredths of a mol., causes a very rapid rise in vapour pressure, equilibrium being rapidly attained. On account of this, the dissociation pressures of the hexammoniates could not be accurately determined. These ammoniates may be compared with the zeolites, which, unlike normal hydrates, lose water very rapidly. The phenomenon has not been observed with other ammoniates.

Magnesium chloride and bromide both form a diammoniate and a monoammoniate, the iodide forms only a diammoniate. The table gives the heats of formation in Cals. and the absolute temperatures at which the dissociation pressure is 100 mm.

| | Saturated mixed crystals. | $2NH_3$. | $1NH_3$. |
|---|---|---|---|
| $MgCl_2$ | 13·3; 367° | 17·9; 495° | 20·8; 573° |
| $MgBr_2$ | 15·2; 420° | 20·1; 559° | 21·7; 606° |
| $MgI_2$ | 17·2; 475° | 22·7; 636° | — |

E. H. R.

**The Solidification Diagram of the Zinc–Arsenic Alloys.** W. Heike (*Z. anorg. Chem.*, 1921, **118**, 264—268).—Thermal examination was made of alloys containing from 6·6 to 92% of arsenic and with the aid of the results the equilibrium diagram was constructed. Two compounds, both melting without decomposition, are formed, $Zn_3As_2$, m. p. 1015°, and $ZnAs_2$, m. p. 771°; the former has a transition point at 671°. With excess of zinc, pure zinc appears with $Zn_3As_2$, no solid solutions being formed. Arsenic dissolves little zinc, but on the other hand is soluble to a considerable extent in the compound $ZnAs_2$. Two eutectics are formed, at 62% and 81·5% As respectively, the corresponding temperatures being 730° and 723°. Both compounds are very brittle,

and $ZnAs_2$ shows a well-marked cleavage. This compound always shows super-cooling during crystallisation of the alloys.

E. H. R.

**The Fusion Diagram of $Cd(NO_3)_2,4H_2O+Ca(NO_3)_2,4H_2O$ at Pressures of 1 to 3000 kilo./cm.$^2$.** MEINHARD HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 313—324).—The fusion diagram of the system $Cd(NO_3)_2,4H_2O+Ca(NO_3)_2,4H_2O$ at the normal pressure has been previously determined (A., 1913, ii, 484). It was shown that the stable form of calcium nitrate forms a eutectic with cadmium nitrate at 91% $Ca(NO_3)_2,4H_2O$ and 40·6°, whilst the unstable form of the calcium salt forms a continuous series of mixed crystals with the cadmium salt. The effect of increased pressure up to 3000 kilos. per sq. cm. on the diagram has now been investigated. The general form of the diagram is unchanged. The *p–t* curve for mixed crystals containing a high proportion of the calcium salt could not be followed at higher pressures on account of the rapid change of the calcinm salt into the stable form. Excess of the cadmium salt inhibits this change, but as the pressure increases, more cadmium salt is needed to produce this effect. With increasing pressure, the m. p. of the stable calcium salt rises much more rapidly than that of the unstable. The latter does not form mixed crystals with cadmium nitrate. The lowering of the m. p. of the stable calcium salt by the cadmium salt is independent of the pressure. With increasing pressure, the eutectic point moves towards the cadmium side; at 1000 kilo./cm.$^2$ it is at 79% calcium nitrate, 47·8°; at 2000 kilo./cm.$^2$, 74% and 55°, and at 3000 kilo./cm.$^2$, 71% calcium nitrate and 61·5°.

E. H. R.

**Light Reactions of the Oxides of Titanium, Cerium, and the Earth Acids.** CARL RENZ (*Helv. Chim. Acta*, 1921, **4**, 961—968; cf. A., 1921, ii, 316).—Titanium dioxide, cerium dioxide, niobium pentoxide, and tantalum pentoxide are in themselves stable towards light, but become markedly photosensitive in the presence of suitable media. Reaction is due to reduction; this is the more remarkahle since the oxides are reducible by purely chemical means with considerable difficulty.

Titanium dioxide, niobium pentoxide, and, to a less degree, cerium dioxide undergo reduction when exposed to light in the presence of certain organic liquids and reducing solutions, particularly glycerol. A lower oxide appears to be formed (zirconium dioxide is not photosensitive and does not form a lower oxide) which on exposure to air or on being heated regenerates the original material. In the case of niobium pentoxide, the process depends to some extent on the presence of impurities, notably stannic and tungstic acids, zirconium compounds, and titanic acid or its anhydrides. Brown vanadium pentoxide becomes black with greater or less rapidity when exposed to light beneath glycerol, benzaldehyde, cinnamaldehyde, cuminol, or aqueous mannitol solution; a lower oxide, initially vanadium tetroxide, is produced. Solutions of citric or tartaric acid in absolute alcohol become green

and ultimately blue when illuminated in the presence of vanadium pentoxide; carbon dioxide is evolved freely. Similar decomposition is observed with mandelic acid, but, in this instance, the vanadium pentoxide is blackened. Brown neodymium oxide containing praseodymium does not alter in appearance when illuminated under glycerol or phenylhydrazine; it becomes bluish-grey when warmed with the latter, owing to conversion of the brown to the yellow oxide of praseodymium. When exposed to sunlight in the presence of glycerol, benzaldehyde or tartaric acid dissolved in alcohol, bismuth oxide becomes grey and ultimately dark black. Reduction to the lower oxide and, possibly, to the metal takes place. In similar circumstances, antimony trioxide is also photosensitive. H. W.

**Concentration of the Erbium Earths.** PAUL H. M.-P. BRINTON and C. JAMES (*J. Amer. Chem. Soc.*, 1921, **43**, 1397—1401).—*Four methods for the concentration of the less basic of the rare earths have been investigated*; the methods examined are: (1) formation of basic nitrates, (2) crystallisation of chlorides from 1 : 1-hydrochloric acid, (3) formation of basic chlorides, and (4) formation of basic thiosulphates. The authors highly recommend the first method for the separation of erbium, holmium, dysprosium, and the less basic earths from yttrium, and the second method for the separation of holmium and dysprosium from yttrium. The basic nitrate formation was carried out with (*a*) a solution of yttrium nitrate containing a little erbium, and (*b*) a yttrium–erbium–holmium mixture. In the former case, the solution was boiled and treated with a fairly concentrated solution of sodium hydroxide and thoroughly boiled. The yttrium hydroxide which first precipitated soon dissolved. The addition of sodium hydroxide was continued until minute crystals of the basic nitrate were observed swirling through the liquid. The whole was then set aside to cool, when a mass of needle-like crystals of the basic nitrate was obtained. These were collected, dissolved in the least amount of nitric acid, and treated with sodium hydroxide solution as before. The basic nitrate crystals from this when dissolved in nitric acid gave a rose-red solution which exhibited intense absorption bands of erbium, thus showing that the erbium was rapidly collecting in this fraction. The original filtrate was treated several times with sodium hydroxide, and although the concentration of nitrates was kept high the erbium absorption bands soon began to fade. The results obtained with the second mixture were equally good. The crystallisation of the chlorides was effected with a solution containing yttrium, holmium, and dysprosium. The solution in hydrochloric acid was boiled down until acid of constant boiling point was obtained. The solution was then evaporated until a scum appeared on the surface, when it was set aside for fifteen to twenty hours. The crystals were separated by decantation and the crystallisation proceeded with; by the time the tail fraction had become No. 9 and the head fraction No. 4 owing to the combination of small

head fractions, it was found that the atomic weights had become 92·5 and 124·0 respectively. After four further fractionations the atomic weight of the tail fraction No. 12 was 91·5 whilst that of the head fraction No. 4 was 133·70. The order of separation in order of decreasing solubility of the chlorides is erbium, yttrium, holmium, dysprosium. J. F. S.

**Disglomeration and Formation of the Autogenous Lead Tree.** A. Thiel (*Ber.*, 1921, **54**, [*B*], 2755—2758; cf. A., 1920, ii, 622).—Disglomeration, which has been observed previously in the cases of lead and copper, is also exhibited by tin when the latter is preserved for some time under stannous chloride solution in a loosely stoppered bottle.

Large uniform crystals of lead become strongly corroded when preserved for some weeks beneath Heller's solution; a considerable quantity of lead powder is formed but, as expected, there is no evidence of disglomeration, that is, formation of deep fissures at the boundaries of the crystallites. Unexpectedly in the light of the previous theory, the large crystallites readily exhibit the formation of the lead tree when preserved beneath a solution of lead nitrate acidified with nitric acid. The phenomenon is observed only after the formation of a white skin of basic salt on the metal and is explained in the following manner. The presence of the skin inhibits the contact of dissolved lead salt and metal by convection and greatly impedes the diffusion of the lead ion. Beneath the skin, therefore, the solution soon contains practically only lead nitrate and is poor in lead ions, whereas the external solution still contains lead nitrate and therefore has a much higher lead ion concentration. The possibility of the formation of a short-circuited concentration cell is thus provided. H. W.

**The Chemical Behaviour of Crystallised Binary Compounds with one Component Nobler than Hydrogen.** G. Tammann (*Z. anorg. Chem.*, 1921, **118**, 93—104).—The author draws a comparison between metallic mixed crystal series and binary compounds. In the former case, the members of a mixed crystal series behave chemically and electrically in a similar manner to one or other component, according to the proportion of each present, with sharply defined limits at molecular fractions which are generally a simple multiple of 1/8. This behaviour is correlated with the lattice structure of the mixed crystals, and may be expected also in crystallised binary compounds which have a similar lattice structure, the difference being that in the latter case the proportions of the two kinds of atom are fixed. It is to be expected that binary compounds will show similarity chemically or electrically to one or other component, and when two or more compounds of the two elements are formed, some will resemble one component and some the other. As an example confirming this view, the compounds of lead and palladium are cited. In this series the compounds $Pb_2Pd$, $PbPd$, $PbPd_2$, and $PbPd_3$ have been identified. In a solution of lead nitrate against

lead these all give a potential equal to that of palladium, but as soon as any free lead is present the potential drops to zero. Chemically, all the palladium–lead compounds are as resistant as palladium. Binary compounds can be conveniently classed as resistant or non-resistant, the former showing the properties of the nobler, the latter those of the baser component.

The above principles are applied to the discussion of a large number of binary compounds, principally metallic, such as those present in alloys of gold, silver, copper, and platinum, besides sulphides, silicides, and carbides, and it is shown that the compounds can be classified as resistant or non-resistant. The more base the inactive component is, the greater is the number of atoms of the nobler component necessary to protect it. In general, a smaller number of gold than of silver atoms are needed to protect a given atom of a baser metal. These considerations apply to compounds in which one component is nobler than hydrogen. When both are less noble than hydrogen, the classification into resistant and non-resistant does not apply, since both constituents and their compounds decompose water. Apart from compounds of this type, it is possible, in a series of binary crystallised conglomerates, to determine from a few measurements of their galvanic potential which of the components they will resemble in their chemical character. E. H. R.

**The Chemical and Electrical Behaviour of some Series of Alloys.** WILHELM JENGE (*Z. anorg. Chem.*, 1921, **118**, 105—122).—With a view to test the theory put forward by Tammann (preceding abstract) that crystallised binary compounds, when no diffusion of the atoms is possible, may be expected to behave chemically and electrically as one or other of the constituent elements a number of series of alloys, in which binary compounds are formed, were examined. The alloys were used as anodes and subjected to the action of halogen, sulphate, or nitrate ions, and were tested against acids and alkalis. In the cobalt–silicon series, in which the compounds formed are $Co_2Si$, $Co_3Si_2$, CoSi, $CoSi_2$, $CoSi_3$, those having less than 32% of silicon were readily attacked by acidic ions, but those with higher silicon content were resistant. That is to say, CoSi and the higher silicides behave as silicon, the other compounds as cobalt. Towards cold acids, the same compounds were respectively resistant and non-resistant and towards cold alkalis all were resistant except $CoSi_3$, the behaviour of which resembled that of silicon. No sharp demarcation of properties was found in the behaviour of the alloys towards hot acids and alkalis because the cobalt loses its passivity and decomposes water. In the series of nickel–silicon alloys somewhat similar results were obtained, but the compound NiSi, unlike CoSi, was not resistant to halogen ions. In the manganese–silicon series only $Mn_2Si$ was non-resistant to acids and all, that is, $Mn_2Si$, $Mn_xSi_y$, and MnSi were resistant to sodium hydroxide.

Alloys of antimony with cadmium and tin and of bismuth with thallium were also examined. The compounds $Cd_3Sb_2$ and $Zn_3Sb_2$

have the potentials of cadmium and tin respectively, whilst CdSb and ZnSb soon approximate to the hydrogen potential. The cadmium alloys precipitate antimony and lead from solution, and $Zn_3Sb_2$ precipitates not only lead, but also cadmium. A bismuth-thallium alloy with the composition $Bi_5Tl_3$ gives the hydrogen potential, but after etching with hydrochloric acid, the bismuth potential, indicating that the surface thallium atoms have been removed, leaving only bismuth exposed.

Of the lead-thallium alloys, those with over 0·49 mol. of lead show the lead potential, those with 0 to 0·475 mol. of lead show the thallium potential.

Great difficulty was experienced in measuring the potentials of the alloys of magnesium with copper, lead, cadmium, and tin, but it appears that at the moment of contact with the electrolyte they have the magnesium potential, which, however, rapidly falls.

E. H. R.

**Physical Chemistry of the Oxides of Lead. II. The Supposed Enantiotropy of Lead Monoxide.** SAMUEL GLASSTONE (T., 1921, **119**, 1914—1927).

**Binary Systems of the Sulphates, Chromates, Molybdates, and Tungstates of Lead.** F. M. JAEGER and H. C. GERMS (*Z. anorg. Chem.*, 1921, **119**, 145—173).—The paper comprises an account of thermal investigations of the binary systems of PbO with $SO_3$, $CrO_3$, $MoO_3$, and $WO_3$ respectively, and of the different systems formed by pairs of the compounds $PbSO_4$, $PbCrO_4$, $PbMoO_4$, and $PbWO_4$. By an optical method the transition temperature of PbO from the red, tetragonal, low temperature form to the yellow, rhombic, high temperature modification was found to be 587°. The melting point of pure lead oxide is 879°. The following melting points were also freshly determined, and differ slightly from accepted values: chromium trioxide, 198°; molybdenum trioxide, 795°; tungsten trioxide, 1473°. The examination of the binary systems formed by lead monoxide with the acid anhydrides was limited in each case to the partial system $PbO–PbM'''O_4$. In the system $PbO–PbSO_4$, the existence of the following compounds was recognised: $Pb_4SO_7$, $Pb_3SO_6$, $Pb_2SO_5$, $PbSO_4$. The first has no real melting point, but decomposes at 897°, forming $Pb_3SO_6$, m. p. 961°, which has a transition point at 450°. $Pb_2SO_5$ (lanarkite) has m. p. 977°. $PbSO_4$ decomposes markedly at 1135° and its m. p. is estimated by extrapolation to be 1170°. The transition point of $PbSO_4$ from the β to the low temperature α form is 864±1°. Three eutectics are formed at 89 mols. % PbO and 835°, 60 mols. % PbO and 950°, and 34 mols. % PbO and 960°.

In the system $PbO–PbCrO_4$, the compounds $Pb_5CrO_8$, $Pb_7Cr_2O_{13}$, $Pb_2CrO_5$, and $PbCrO_4$ were recognised. The first has no real melting point and exists only below 815°. $Pb_7Cr_2O_{13}$, m. p. 854°, has a reversible transition point at 744°, and forms with $Pb_5CrO_8$, m. p. 920°, a eutectic at 68 mols. % PbO and 841°. Lead chromate, $PbCrO_4$, is found to be trimorphous; the α-form

is stable below 707°; the β-form between 707° and 783°, and th γ-form above 783°, melting at about 844° with evolution of oxyger The heat effect of the change $\alpha \rightleftharpoons \beta$ is small and is sharper i binary mixtures with lead oxide than in the pure substance. Th eutectic between $PbCrO_4$ and $Pb_2CrO_5$ occurs at 820°, but thi part of the equilibrium diagram could not be determined accuratel on account of decomposition.

The system $PbO$–$PbMoO_4$ shows only two compounds, $Pb_2MoO$ m. p. 951°, and $PbMoO_4$, m. p. 1065°. There are two eutectic at 87·5 mols. % PbO, 762°, and at 40 mols. % PbO, 933°. Tl tungstates correspond with the molybdates, $Pb_2WO_5$, m. p. 899 and $PbWO_4$, m. p. 1123°, with a transition point at 877°.

*The equilibrium diagram for the system* $PbCrO_4$–$PbSO_4$ *largely conjectural owing to the considerable amount of decomp sition occurring at higher temperatures. There is a gap in tl mixed crystal series between about 40% and 30%* $PbCrO_4$. Tl mixed crystals have transition points at 934°, 874°, and 74ε In the $PbSO_4$–$PbMoO_4$ system mixed crystals are formed co taining up to 6 mols. % sulphate or 2 mols. % molybdate. The is a eutectic at 57 mols. % molybdate and 962°. At 879°, t mixed crystals have a transition point. In the $PbSO_4$–PbW system the mixed crystals of the β-type separating at the eutec temperature contain respectively 37 mols. % sulphate and 7 mols. tungstate. The eutectic is at 51 mols. % tungstate and 99 At 875° occurs the $\beta \rightleftharpoons \alpha$-sulphate transformation and at 8 the corresponding tungstate change. The $PbCrO_4$–PbMo diagram is largely hypothetical. The composition of the limiti mixed crystals on the molybdate side is 48 mols. % $PbCrO_4$ 838°, the eutectic temperature. Transitions occur at 799° $\gamma \rightarrow \beta$-chromate mixed crystals, and at 697° $\beta \rightarrow \alpha$. In t $PbCrO_4$–$PbWO_4$ system the eutectic temperature is 837° and t limiting mixed crystals on the tungstate side contain 41 mols. $PbCrO_4$. *Lead molybdate and lead tungstate form an isodim phous mixed crystal series with a transition temperature at 108 A mixture containing 75 mols. %* $PbMoO_4$ *is in equilibrium* this temperature with both kinds of mixed crystal. E. H. R

**Photochemistry of Thallous Chloride. II.** CARL RI (*Helv. Chim. Acta*, 1921, **4**, 950—960).—A continuation of previ work (A., 1920, ii, 71). Thoroughly illuminated, blackish-bro thallous chloride, in consequence of photolysis, contains as prim product more or less grey to slate-grey photothallous chlori in addition to yellow intermediate thallous–thallic chlorides forn in accordance with the scheme: 6TlCl+Light=photochlorid $TlCl_3,3TlCl$. Thallic hydroxide, formed by subsidiary actions also present. These phases characterise the photo-processes those cases in which the change of colour extends over the sc greyish-brown, dark greyish-brown, blackish-brown, and he occur when thallous chloride is illuminated in the dry condit under water, and in the presence of solutions of many neu salts. In the presence of reducing agents or of organic hydrc

acids, the action of light on thallous chloride only leads to the production of the photochloride. The formation of thallous–thallic chlorides is not observed in the presence of alkalis or alkali carbonates, which decompose these compounds immediately. The production of photothallous chlorides and of thallic hydroxide does not occur in the presence of hydrochloric acid, even without the addition of organic substances.

Photothallous chloride can be prepared by purely chemical methods if ferrous sulphate is added to a boiling, saturated aqueous solution of thallous chloride and the mixture is treated with an excess of ammonia. The black precipitate of photothallous chloride and iron hydroxides is allowed to settle, and is subsequently washed with hydrochloric acid until the iron compounds are dissolved; the slate-grey photothallous chloride so obtained behaves in exactly the same manner as the photosynthetic product.

H. W.

**Ammoniates of Cupro- and Thallo-haloids.** WILHELM LTZ and *WILHELM STOLLENWERK* (*Z. anorg. Chem.*, 1921, **119**, —114).—The formation and vapour pressures at different mperatures of ammoniates of cuprous and thallous chloride, omide, and iodide were investigated, using apparatus similar that employed in experiments on the ammoniates of silver loids (A., 1921, ii, 201). When saturated with ammonia gas, prous chloride first shrinks to a yellow mass, then swells and comes greyish-white. Saturation at −70° to −30° requires at ist a day. When the excess of ammonia is allowed to evaporate room temperature and atmospheric pressure, cuprous chloride iammoniate remains. In damp air, it quickly turns green. ie pressure isotherms also indicate the existence of a sesquiamoniate and a monammoniate. Cuprous bromide behaves nilarly, forming a white triammoniate, a sesquiammoniate, and monammoniate. Cuprous iodide absorbs ammonia quickly at om temperature. It forms four compounds, containing reectively 3, 2, 1, and ½ mol. of ammonia. In the following table e given the heats of formation $Q$ in Cals. and the temperatures absolute degrees at which the dissociation pressures of all these mpounds are equal to 100 mm.

| | $3NH_3$. | $2NH_3$. | $1\frac{1}{2}NH_3$. | $1NH_3$. | $\frac{1}{2}NH_3$. |
|---|---|---|---|---|---|
| CuCl | 9·48; 283° | — | 12·61; 326° | 16·73; 417·5° | — |
| CuBr | 9·50; 283° | — | 13·15; 339° | 14·64; 369·0° | — |
| CuI | 10·37; 286·5° | 11·30; 298° | — | 14·70; 371·0° | 15·22; 390° |

Thallous haloids do not absorb ammonia at the ordinary temrature, but in liquid ammonia they all form triammoniates. ie vapour pressures are all very close to those of ammonia itself. ie triammoniates are soluble to a certain extent in liquid ammonia, e solubility increasing with rising temperature and with the omic weight of the halogen. The heat of formation is about Cal. for the ammonia compound of each of the three haloids. lower ammoniates are formed.

E. H. R.

**The Action of Molten Alkali Chlorides on Copper O** J. ARVID HEDVALL and GUNNAR BOOBERG (*Z. anorg. Chem.*, **119**, 213—216).—It was shown in a former paper (Hedva Heuberger, A., 1921, ii, 508) that potassium chloride could r used as a flux in the fusion of cupric oxide with aluminium on account of a reaction taking place between the pota chloride and copper aluminate. It is now shown that when c oxide is heated with potassium chloride, cuprous oxide is f and oxygen evolved. This is best demonstrated by adding oxide in small quantities to a mixture of potassium and so chlorides at 1000° and continuing the heating for one and hours. At the same time, a basic cupric chloride is formed by prolonged heating with sodium or potassium chloride sol is obtained as the compound $3CuO,CuCl_2,4H_2O$. E. H.

**Phenomena of Diffusion in Metals in the Solid Stat Cementation of Non-ferrous Metals. I. Cementatic Copper by means of Ferro-manganese.** G. SIROVICH A. CARTOCETI (*Gazzetta*, 1921, **51**, ii, 245—261).—A bar of c was arranged centrally in a porcelain tube glazed internally a tube then packed with ferro-manganese containing 5% of charcoal, both these materials being capable of passing thro sieve with 64 meshes per sq. cm. and of being retained by 324 meshes per sq. cm. The tube was closed by means of r stoppers luted with sodium silicate, one of the stoppers havin holes to admit a thermo-couple for measuring the tempe and a glass tube bent at right angles and with its end dippin mercury. After the tube had been heated for some hours a in a Heraeus furnace, considerable proportions of the mang were found to have penetrated the copper (cf. *J. Soc. Chem.* 1922, 17A). T. H.

**Tervalent Copper.** G. SCAGLIARINI and G. TORELLI (*Ga* 1921, **51**, ii, 225—228).—Contrary to Moser's statement (A., ii, 549), the action of potassium persulphate on cupric hyd in presence of barium hydroxide at temperatures obtain cooling with ice and salt results in various changes in the of the solution and in the deposition of a tenuous amaran precipitate, which may be purified by repeated washing wit water by decantation. The compound thus obtained yields o when treated with sulphuric acid, oxidises hydrochloric acid liberation of chlorine, oxidises ammonia in the cold with prod of nitrogen, nitrous acid, and traces of nitric acid, decolorise manganate, and decomposes potassium iodide with liberati iodine in quantity greater than that corresponding with the portion of copper present. Since it does not yield hydrogen per when treated with dilute acid, the compound lacks the gro characteristic of peroxides and is thus different from the o yellow copper peroxide obtained by means of hydrogen pero The ratio between the percentages of copper and active o present is in agreement with the formula $Cu_2O_3$. T. H.

**Production of Single Crystals of Aluminium and their Tensile Properties.** H. C. H. CARPENTER and CONSTANCE F. ELAM *Proc. Roy. Soc.*, 1921, [*A*], **100**, 329—353; cf. A., 1921, ii, 641).—A continuation of work previously published (*loc. cit.*) on the production of large crystals of aluminium. The metal used in the present work had a purity of 99·6%, the impurity being 0·19% silicon and 0·14% iron. The test-pieces used were 70 mm. with a parallel portion 103 mm. long, 26 mm. broad, and 3 mm. thick, and were estimated to contain 1,687,000 small crystals in the parallel portion (103×26×3 mm.). The authors first describe the treatment necessary to convert the whole of the crystals into a single crystal. Three separate processes are shown to be necessary: (i) the aluminium strip is heated at 550° for six hours, (ii) the strip after cooling is subjected to a stress which is equivalent to 378 kilos. per sq. cm., and gives an average elongation of 1·6% on 76 mm., (iii) the test-piece is finally placed in a furnace at 450° and the temperature raised 15—20° per day up to 550° and then for 1 hour at 600°. Applying this treatment to thirty-eight test pieces showed that nine pieces consisted of a single crystal, fourteen of two crystals, nine of three crystals, four of four crystals, and two of six crystals. The tensile strength of aluminium strips consisting of known numbers of crystals has been determined. It is shown that for strips consisting of 150 crystals per 25 mm. it is 708—740 kilos. per sq. cm., and these give an elongation of 36—38% on 76 mm. The tensile strength of strips consisting of a single crystal varies between 598 and 642 kilos. per sq. cm. and these strips suffer an elongation of 4—86% on 76 mm. The varying tensile strength and elongation was accompanied by differences in the type of stretching and fracture. Strips consisting of two crystals have a tensile strength of 441—550 kilos. per sq. cm. and suffer an elongation of 29—70% on 76 mm., whilst strips consisting of three crystals have a tensile strength of 456—567 kilos. per sq. cm. and suffer an elongation of 6—55% on 76 mm. A further series of experiments on the production of single crystals in bars is described. J. F. S.

**The Thermal Treatment of certain Complex Aluminium Alloys.** LÉON GUILLET (*Compt. rend.*, 1921, **173**, 979—982).—In order to determine the effect of each constituent on the behaviour of duralumin under thermal treatment (cf. *ibid.*, 1919, **169**, 508), the author has studied alloys of aluminium and copper, aluminium and silicon, aluminium, silicon, and copper, aluminium, magnesium, and silicon, and quaternary alloys containing all four elements. Measurements of hardness have been made on annealed samples, and on samples tempered at different temperatures, the measurements being made in the latter case immediately after tempering and also after the alloy had been kept for forty-eight hours at 20°. From the results of these measurements and from micrographic examinations of the alloys it is shown that the simultaneous presence of silicon, magnesium, and copper is indispensable to obtain the interesting results given by tempering high resistance aluminium alloys. W. G.

**Solubility Limits of Carbon in Ternary Steels. I. The System Chromium–Iron–Carbon.** KARL DAEVES (*Z. anorg. Chem.*, 1921, **118**, 55—66).—Experiments were made to determine the influence of chromium on the solubility of carbon in iron and to determine the position of the corresponding solubility line in the ternary chromium–iron–carbon diagram. The solubility falls off rapidly at first as the chromium content increases, then more slowly, the general form of the curve being hyperbolic. Points on the curve were determined by observing what chromium content was necessary, with a given carbon content, to cause the appearance of a eutectic in the structure of the metal. To make the hard alloys workable, for the preparation of polished surfaces, it was necessary to heat for several hours at 800°, just below the $Ac_1$ point, by which treatment the solid solution was broken up and the metal softened. Etching was accomplished by electrolysis in ammonium persulphate solution. In eutectoid alloys, the cementite is practically unattacked by hot sodium picrate solution. Cold alkaline potassium ferricyanide turns the hard constituent of the eutectic brown to yellow, leaving the mixed crystals untouched. The solubility curve explains many of the known properties of chromium steels. The melting point of steel and the arrest points are little affected by chromium up to 10%. [*Cf. J. Soc. Chem. Ind.*, 1922, 16A.] E. H. R.

**Solubility Limits of Carbon in Ternary Steels. II. The System Tungsten–Iron–Carbon.** KARL DAEVES (*Z. anorg. Chem.*, 1921, **118**, 67—74).—The effect of tungsten on the solubility of carbon in iron was studied in the same way as that of chromium (preceding abstract), and a solubility curve of similar form was obtained, separating eutectic from non-eutectic steels in the ternary diagram. Sudden changes in the physical properties of tungsten steels are correlated with changes of composition involving the passage from one side to the other of this limiting curve. The appearance of so-called double carbides of iron and chromium or of iron and tungsten, observed by different workers, is attributed to the same cause. Small amounts of tungsten in steel raise the melting point, but larger amounts depress it.

E. H. R.

**The Colour of Iron Alum.** JANE BONNELL and EDGAR PHILIP PERMAN (T., 1921, **119**, 1994—1997).

**Complex Selenates.** JULIUS MEYER (*Z. anorg. Chem.*, 1921, **118**, 1—47).—A large number of new complex selenates and incidentally some simpler compounds which have not hitherto been described, were prepared for comparison with the corresponding sulphates. The new selenates described belong to the chromi- and cobalti-series, and show the closest resemblance to the sulphates, differing from these occasionally only in their water of crystallisation. On account of the ease with which selenic acid is reduced, difficulties were at times encountered in the preparation of certain of the compounds.

[With LEONHARD SPEICH.]—Chromiselenates. Violet chromic selenate, $[Cr(H_2O)_6]_2(SeO_4)_3,3(or\ 4)H_2O$, forms a crystalline powder, readily soluble in water, from which it is precipitated by alcohol or acetic acid. Its aqueous solution dissolves chromic hydroxide with formation of green basic salts. When the violet salt is heated in solution or in the solid state at 90° it changes irreversibly into a green chromiselenate. The green salt prepared in the solid state has the composition $Cr_2(SeO_4)_3,10H_2O$ and dissolves very slowly in water, probably only after addition of water. The green salt may have a constitution of the type $[Cr(SeO_4)(H_2O)_5]_2SeO_4$. When a solution of the violet salt is boiled for some time, a green compound is formed which is precipitated by alcohol as a green oil and dries to an amorphous, green solid. It is very soluble in water and gives no precipitate with barium salts or with ammonia. It is probably a triselenatochromic acid, $[Cr(SeO_4)_3]H_3$.

*Chloropentaquochromiselenate*, $[CrCl(H_2O)_5]SeO_4,3H_2O$, was prepared from chloropentaquochromichloride and sodium selenate; it forms a bright green powder very soluble in water and alcohol. Attempts to obtain other chloro-selenates, corresponding with known chloro-sulphates, were not successful.

*Dichlorotetraquochromihexaquochromiselenate*,

$$[CrCl_2(H_2O)_4](SeO_4)_2[Cr(H_2O)_6],$$

forms a green, crystalline powder, readily soluble in water, slightly so in alcohol. An attempt to prepare a corresponding double chromi-aluminium selenate failed, although sulphates of the type $[CrCl_2(H_2O)_4](SO_4)_2[M(H_2O)_6]$, where M=Cr, Fe, Al, or V, were prepared by Werner and Huber (A., 1906, ii, 170).

*Hexamminechromiselenate*, $[Cr(NH_3)_6]_2(SeO_4)_3$, was prepared from the corresponding nitrate and selenic acid. It is precipitated from aqueous solution by alcohol as a heavy, yellow, finely crystalline powder. The salt is amorphous whilst the corresponding sulphate has $5H_2O$.

*Chloropentamminechromiselenate*, $[CrCl(NH_3)_5]SeO_4$, was prepared from purpureochromichloride and silver selenate. It forms a heavy, red, amorphous powder sparingly soluble in water. The corresponding sulphate is much more soluble, and crystallises with $2H_2O$.

*Hexacarbamidechromiselenate*, $[Cr(NH_2{\cdot}CO{\cdot}NH_2)_6]_2(SeO_4)_3$, prepared from hexacarbamidechromichloride and silver selenate, was obtained as a bright green, finely crystalline powder, moderately soluble in water, from which alcohol precipitates it.

*Triethylenediaminechromiselenate*, $[Cr\ en_3]_2(SeO_4)_3$, from the corresponding chloride and silver selenate, is a reddish-yellow, heavy, crystalline powder, soluble in water and precipitated by alcohol. When the dry salt is heated at 100°, the colour changes to reddish-violet.

*Aluminium selenate*, which has not before been described, forms a white, crystalline powder, easily soluble in water and precipitated by alcohol. It appears to contain less than $18H_2O$, but the analysis did not distinguish between 15 and $17H_2O$.

[With HANNS MOLDENHAUER.]—Complex cobaltiselenates. The

complex cobaltiselenates prepared were confined to those containing only one cobalt complex and to those with 6, 5, or 4 molecules of ammonia or 4 molecules of pyridine.

*Hexammine(luteo)cobaltiselenate*, $[Co(NH_3)_6]_2(SeO_4)_3,5H_2O$, corresponds in every respect with luteocobaltisulphate.

*Aquopentamminecobaltiselenate*, $[Co(H_2O)(NH_3)_5]_2(SeO_4)_3,3H_2O$, was prepared both from the corresponding cobaltichloride and from selenatopentamminecobaltiselenate. The salt is similar in physical and chemical properties to roseocobaltisulphate.

*Diaquotetramminecobaltiselenate*, $[Co(H_2O)_2(NH_3)_4]_2(SeO_4)_3,3H_2O$, was prepared from carbonatotetramminecobaltiselenate and selenic acid. It dissolves in water to a deep red solution from which alcohol precipitates it as a bright red, crystalline powder. It loses its water of crystallisation on exposure to air.

*Chloropentamminecobaltiselenate*, $[CoCl(NH_3)_5]SeO_4$, was prepared from purpureocobaltichloride and silver selenate; it corresponds in its properties with purpureocobaltisulphate.

*Chloroaquotetramminecobaltichloride selenate*,

$$\{[CoCl(H_2O)(NH_3)_4]Cl\}_2SeO_4,$$

was obtained when dichlorotetramminecobaltichloride was treated with silver selenate, through hydration of one of the nuclear chlorine atoms. It forms a violet, crystalline powder, giving a violet aqueous solution.

*Nitropentamminecobaltiselenate*, $[Co(NO_2)(NH_3)_5]SeO_4$, from the corresponding chloride and silver selenate, forms bright yellow, microscopic crystals, giving a yellowish-brown, aqueous solution. It forms a periodide, as does the corresponding sulphate.

*Sulphatopentamminecobaltiselenate*, $[Co(SO_4)(NH_3)_5]_2SeO_4,2H_2O$, was prepared from the corresponding sulphato-bromide and silver selenate. It is precipitated from aqueous solution by alcohol in rose-coloured leaflets consisting of microscopic, rhombic tablets The corresponding sulphatosulphate contains only $1H_2O$.

*Acid selenatopentamminecobaltiselenate*,

$$[Co(SeO_4)(NH_3)_5]SeO_4H,2H_2O,$$

was prepared by treating chloropentamminecobaltichloride with concentrated selenic acid. From the diluted solution the acid salt crystallised in reddish-violet crystal aggregates. It closely resembles the sulphato-sulphate and forms the starting material for the preparation of a series of selenatopentamminecobalti-salts including several of the following.

*Normal selenatopentamminecobaltiselenate*,

$$[Co(SeO_4)(NH_3)_5]_2(SeO_4),H_2O,$$

was obtained by treating the above acid selenate with alcohol it has a brighter red colour than the acid salt.

*Selenatopentamminecobaltisulphate*, $[Co(SeO_4)(NH_3)_5]_2SO_4,H_2O$ was obtained from the selenato-bromide and silver selenate. It is precipitated by alcohol from aqueous solution in bright red, lustrous tablets. This salt is metameric with the above sulphatopentamminecobaltiselenate, but the two are not isomorphous, as the latter crystallises with $2H_2O$.

*Selenatopentamminecobaltinitrate*, $[Co(SeO_4)(NH_3)_5]NO_3$, was pre

pared from the above acid selenate and ammonium nitrate. It separates in well-formed, bright red, sparingly soluble crystals.

*Selenatopentamminecobaltibromide*, $[Co(SeO_4)(NH_3)_5]Br$, was prepared from the above acid selenate and hydrobromic acid. It is thrown down by alcohol from aqueous solution as a bluish-red precipitate.

*Selenatopentamminecobaltihexachloroplatinate*,

$$[Co(SeO_4)(NH_3)_5]_2PtCl_6,2H_2O,$$

forms lustrous, orange-red tablets, sparingly soluble in water.

In the tetramminecobalti-series only carbonic acid of the bivalent acids could be introduced into the complex. With two univalent acid radicles, stereoisomerism becomes possible, and it was found possible to prepare the 1 : 2- and 1 : 6-dinitrotetramminecobaltiselenates.

*Carbonatotetramminecobaltiselenates*, $[Co(CO_3)(NH_3)_4]_2SeO_4,3H_2O$, is similar to the corresponding sulphate, crystallising in dark red leaflets which lose their water of crystallisation on exposure to air.

*Acid dichlorotetramminecobaltiselenate*, $[CoCl_2(NH_3)_4]SeO_4H$, crystallises in dark green, well-formed needles but is unstable and readily changes to the chloroaquotetrammine salt described above.

*Acid dichlorotetrapyridinecobaltiselenate*, $[CoCl_2Py_4]SeO_4H,2H_2O$, is more stable than the dichlorotetrammine salt; it crystallises in lustrous green leaflets. The salt corresponds with the sulphate described by Werner and Feenstra (A., 1906, i, 450).

1 : 2-*Dinitrotetramminecobaltiselenate*, $[Co(NO_2)_2(NH_3)_4]_2SeO_4$, was prepared from flavocobaltinitrate (Jörgensen, A., 1898, ii, 592) and ammonium selenate; it forms dark brown crystals.

1 : 6-*Dinitrotetramminecobaltiselenate*, stereoisomeric with the last, was prepared from croceocobaltichloride (Jörgensen, *loc. cit.*) and silver selenate; it is precipitated from aqueous solution by alcohol in the form of minute, bright yellow crystals.

The electrical conductivities of many of the above salts in aqueous solution were measured at 25° and their magnitudes were found to agree with the constitutions ascribed to the different salts.

E. H. R.

**The Green Colour of Tungsten Trioxide.** J. A. M. van Liempt (*Z. anorg. Chem.*, 1921, **119**, 310—312).—Tungsten trioxide generally has a yellow colour, but is sometimes green. A number of explanations of this phenomenon have been offered, but it is now shown experimentally that the green colour is due to reduction at ordinary temperatures by traces of organic matter to lower oxides. Provided the green oxide has not been ignited, the yellow colour may be restored by heating it in a current of oxygen. E. H. R.

**Chlorination by Mixed Carbon Monoxide and Chlorine.** F. P. Venable and D. H. Jackson (*J. Elisha Mitchell Sci. Soc.*, 1920, **35**, 87—89).—Chlorination is successfully accomplished with a mixture of carbon monoxide and chlorine, containing the former in excess, in the following cases: zirconium dioxide at 480°, stannic

oxide at 400°, *magnesium* oxide at 475°, aluminium oxide at 450° ferric oxide at 460°, chromic oxide at 625°, manganese dioxide a 460°, uranoso-uranic oxide at 500°. With chlorine in excess, th requisite temperature for zirconium dioxide is 425° and for ferri oxide 370°. CHEMICAL ABSTRACTS.

**Antimonic Acid and the Use of Sodium Antimonate i Analysis.** E. S. TOMULA (*Z. anorg. Chem.*, 1921, **118**, 81–92).—The constitution of antimonic acid and of the salts derive from it has never been satisfactorily settled, and an attempt he now been made to solve the problem by the application of physic chemical methods. The conductivity of the potassium salt wa measured at 25° at dilutions from $V=32$ to 1024, and the basicit of the acid, by the Oswald-Walden rule, was found to be 1. Th rules out the possibility that the salt is a pyroantimonat $K_2H_2Sb_2O_7$, and since it gives a solution having an acid reactio it cannot be the metantimonate, $KSbO_3$. It must therefore l the orthoantimonate, $KH_2SbO_4$. Hydrogen-ion determinations in $1/1024N$-solution by the calorimetric method confirmed this vie The dissociation constant at this dilution was found to be $\alpha=0{\cdot}9$ and the hydrogen-ion concentration $C_H=10^{-6{\cdot}3}$. The equivale conductivity of the sodium salt was, on account of its low sol bility, determined only at dilutions $V=512$ and 1024, and w found to be of the same order as, although slightly lower than, th of the potassium salt. The hydrogen-ion concentration at $V=10$ was $C_H=10^{-6{\cdot}4}$, and it is concluded that the two salts have the sar constitution. Delacroix (A., 1898, ii, 340; 1900, ii, 145) a Senderens (A., 1899, ii, 557) both isolated a soluble and an insolul form of antimonic acid, which they called ortho- and pyro-aci but they differed as to which was which. Conductivity expe ments on the potassium salts show that the soluble acid is t ortho-acid, whether prepared by Senderens's or Delacroix's meth It is concluded, however, that a concentrated solution of antimo acid is not a true solution but a supersaturated colloidal pseu solution, from which the acid soon separates in the insoluble for

Determinations were made at 18°, 25°, and 33·5° of the so bility of sodium antimonate in water, in aqueous sodium aceta and in aqueous methyl and ethyl alcohols. Expressed in mg. $Na_2O,Sb_2O_5,6H_2O$ per 100 c.c. of solution, the solubility at 18° in water 56·4, in equal volumes of water and ethyl alcohol 0·1, a in 2·5% sodium acetate 3·1.

The following method is recommended for the estimation antimony as sodium antimonate. The antimony must be alkaline solution as sodium sulphantimonate, $Na_3SbS_4$, and m be free from potassium, since in presence of potassium salts p cipitation is incomplete. The solution is warmed at 80° a stirred while a solution of 30% hydrogen peroxide is run in d by drop until vigorous evolution of oxygen commences, and i then boiled until all oxygen evolution ceases. The alkaline solut is neutralised with acetic acid until it is acid to phenolphthal but still weakly alkaline to litmus. It is stirred a further qua

of an hour and then one-half its volume of 96% alcohol is added, after which stirring is continued for ten minutes. After twelve hours, the crystalline sodium antimonate is filtered, washed on the filter with a solution containing 3 grams of sodium acetate, 3 grams of acetic acid, and 400 c.c. of ethyl alcohol per litre, and finally with 50% alcohol. The dried precipitate is separated from the filter-paper, which is burnt separately, is ignited for fifteen minutes in a porcelain crucible, and weighed as sodium metantimonate, $NaSbO_3$. Special directions are given for procedure when tin is present, as it is then necessary to redissolve and re-precipitate the sodium antimonate. [See also *J. Soc. Chem. Ind.*, 1922, 12A.] E. H. R.

**The Reaction Limit of Chemical Agents on Copper–Gold Alloys and their Galvanic Tension.** G. TAMMANN (*Z. anorg. Chem.*, 1921, **118**, 48—54).—The reaction limit in different copper–gold alloys is reached when the molecular fraction of gold present is 1/8, 2/8, or 4/8, according to the chemical reagent used. The reactivity of the mixed crystals may be regarded as due to the loosening of the copper atoms from their lattice combination by the chemical agent or, from another point of view, to the action of the chemical agent on copper atoms which have become detached from the lattice on account of their solution tension. From the latter point of view it was important to determine how the solution tension of the alloys varied with the composition. Measurements were made against a gold electrode in a number of electrolytes, and against silver with silver sulphate as electrolyte. The results showed that the limiting composition beyond which no copper ions appear in the solution and the alloy behaves electrically as pure gold, is at 2/8 mol. fraction of gold. This method does not give such sharp limiting values as the chemical method, however, owing to the sensitiveness of the galvanic tension to impurities on the surface of the metal. The case of the cell silver | saturated silver sulphate | copper–gold is specially interesting, since, when the proportion of gold in the alloy does not exceed 0·145 mol., silver is visibly precipitated and the metal becomes negatively charged, whilst the alloys richer in gold do not precipitate silver and assume a weak positive charge. This weak positive charge indicates a superficial deposit of silver, so that the surface acts as a silver–gold alloy of corresponding composition. It is shown, from consideration of the mixed crystal lattice, that when 1/8 mol. of gold or less is present in the copper alloy, conditions are favourable for the formation of silver crystals. It is suggested that those agents which find their active limit at 2/8 mol. of gold, corresponding with the solution tension limit for copper ions, act first on the copper ions in solution, but as soon as the osmotic pressure of the copper ions exceeds the solution tension, the agent attacks the mixed crystal surface.

E. H. R.

**Ruthenium Tetroxide.** F. KRAUSS (*Z. anorg. Chem.*, 1921, **119**, 217—220).—An aqueous solution of ruthenium tetroxide has

apparently a weak acid reaction, although this is difficult to demonstrate on account of the rapid decomposition of dyes by the solution. The solution behaves as an electrolyte, and is decomposed by the current with formation of a green colour. With alkali hydroxides it forms salts, but only the ammonium salt could be obtained in the pure state. It was prepared by adding concentrated ammonia to a concentrated solution of ruthenium tetroxide in water until the colour changed from yellow to greyish-brown. By evaporating a salt of the composition $(NH_4)_2RuO_5$ was obtained. Under certair conditions, which could not be accurately determined, a mono and a di-hydrate of this salt were obtained. In the preparatior of ruthenium tetroxide, besides the yellow compound, a brownish red substance was observed, less soluble in water than the tetroxide This has not been identified. Ruthenium tetroxide can be estimated by distilling it in a current of dry air at 15° into a speciall constructed weighed flask, dissolving in a little water, reducin with alcohol, evaporating with dilute hydrochloric acid, ignitin in a stream of hydrogen, and weighing the ruthenium. E. H. R.

## Mineralogical Chemistry.

**Native Antimony from Kern County, California.** C. I BEHRE, JUN. (*Amer. J. Sci.*, 1921, [v], **2**, 330—333).—A statemer of the results of an examination of nodular masses of antimon with a crust of oxidation products. L. J. S.

**Identity of Flagstaffite with Terpin Hydrate.** F. N. GUII (*Amer. Min.*, 1921, **6**, 133—135).—A comparison of the cryst constants of flagstaffite (A., 1921, ii, 51) with those of terpin hydra suggests the identity of these; and this is confirmed by comparati tests made on the natural and artificial materials. Variable resul for the m. p. are obtained, owing to loss of water before meltin When heated very slowly the crystals soften at about 100°, a finally melt near 116°. Anhydrous terpin from flagstaffite h m. p. 105°. The terpin hydrate formula, $C_{10}H_{20}O_2,H_2O$, is adopte since the material analysed had been partly dehydrated remaining over sulphuric acid. L. J. S.

**The Natural Iron Hydroxides.** KARL WILLMANN (*Cen Min.*, 1921, 673—678).—A review is given of the colloidal a crystalline forms of iron hydroxides. The scaly (Rubinglimm and acicular (Samtblende or needle-iron-ore) forms of goeth differ in optical characters and are regarded as dimorphous for of $Fe_2O_3,H_2O$. New analyses of Rubinglimmer from the Eleon mine near Giessen gave $Fe_2O_3$ 89·90, $H_2O$ 10·77=100·67, a at $Fe_2O_3$ 88·11, $H_2O$ 11·97=100·08, agreeing with this formula. L. J. S

**Curite, a New Radioactive Mineral.** ALFRED SCHOEP (*Compt. rend.*, 1921, **173**, 1186—1187).—The new mineral is found at Kasolo, Katanga, Belgian Congo, as translucent, reddish-brown, acicular crystals on torbernite or as compact or earthy masses, and consists of minute needles with straight optical extinction. It is readily soluble in cold nitric acid and in hot hydrochloric acid; when heated, it turns dark brown. Analysis gives the formula $PbO,5UO_3,4H_2O$.

| PbO. | $UO_3$. | $H_2O$. | $Fe_2O_3$. | Total. | $d^{17}$ |
|---|---|---|---|---|---|
| 21·32 | 74·22 | 4·00 | 0·17 | 99·71 | 7·192 |

L. J. S.

## Analytical Chemistry.

**The Conditions for the Maximum Precipitation of an Amphoteric Electrolyte.** ADA PRINS (*Chem. Weekblad*, 1921, **18**, 657—658).—The minimum solubility occurs at a definite hydroxyl-ion concentration depending for each amphoteric electrolyte on its solubility product as base and as acid. The concentrations of the positive and negative ions are inversely proportional to their charges. S. I. L.

**Use of Cæsium Chloride in Microchemistry.** ENRIQUE HERRERO DUCLOUX (*Anal. Asoc. Quim. Argentina*, 1921, **9**, 215—227).—Cæsium chloride may be used as a reagent in microchemistry by reason of the well-defined double chlorides which it forms with different metals. Crystallographie descriptions, with photomicrographs, are given of the double salts thus formed with silver, mercury, lead, platinum, gold, palladium, arsenic, antimony, cadmium, tin, copper, aluminium, iron, zinc, nickel, cobalt, manganese, calcium, magnesium, thallium, cerium, and indium.

G. W. R.

**Use of the Zeiss Water Interferometer (Rayleigh-Löwe) for the Analysis of Non-aqueous Solutions.** ERNST COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 114—122).—A description of the Rayleigh-Löwe water interferometer and the method of use for estimating the concentration of aqueous solutions are given. The accuracy obtainable with this instrument is about 99·9998% for aqueous solutions. To use this instrument for non-aqueous solutions greater precautions in the fixing of the temperature are required. The thermostat liquid should also be chosen so as to have a refractive index of the same order as that of the solvent used. When these precautions are taken an accuracy equal to that obtained for water solutions may be obtained with solutions in organic solvents. J. F. S.

**A Buffer Solution for Colorimetric Comparison.** T. C. McIlvaine (*J. Biol. Chem.*, 1921, **49**, 183—186).—The author covers the whole range from $P_H$ 2·2 to $P_H$ 8·0 by mixing two solutions only, viz. a 0·2*M*-disodium phosphate solution with 0·1*M*-citric acid. A table to obtain any desired $P_H$ is given and also a graph.

G. B.

**A Simplified Form of Apparatus for Air Analysis.** Charles Claude Guthrie (*J. Biol. Chem.*, 1921, **48**, 365—371).—The apparatus, which is illustrated in the original, "differs from the well known forms in dimensions rather than in principles or in design."

E. S.

**Estimation of the Gases of the Blood.** Donald D. Van Slyke and William C. Stadie (*J. Biol. Chem.*, 1921, **49**, 1—42).—Improvements in the technique of using the apparatus previously described for the extraction from the blood and measuring of the carbon dioxide (A., 1917, ii, 422—423), oxygen (A., 1918, ii, 82), and carbon monoxide (A., 1920, ii, 53). All the gases can now be estimated in 1 c.c. of blood by a modified form of the original apparatus with narrow measuring tube enclosed in a water-jacket. In the oxygen estimation, the blood is now laked with water, and the amount of ferricyanide has been greatly reduced; the results are about 5% higher than those obtained by Haldane's method. Particularly in the case of the carbon dioxide estimation, the errors are fully analysed, and examples of calculations are given.

G. B

***Mechanical Shaker and other Devices for Use with the* Van Slyke Blood Gas Apparatus.** William C. Stadie (*J. Biol. Chem.*, 1921, **49**, 43—46; cf. preceding abstract).—A motor-driven shaker, a levelling scale, and tonometer rotator are described with the help of figures.

G. B.

**Estimation of Chlorine in Benzaldehyde.** Schimmel & Co. (*Ber. Schimmel & Co.*, 1921, 56—61; from *Chem. Zentr.*, 1921, iv, 771).—Benzaldehyde is burnt in a small lamp so constructed that the amount of liquid burnt may be found by weighing at the beginning and end of the experiment. The products of combustion are passed through two U-tubes containing glass beads moistened with 0·02*N*-potassium hydroxide solution, foaming being prevented by the use of a few drops of petroleum. The washings from the absorption apparatus are united and, after addition of an equivalent amount of 0·02*N*-sulphuric acid, concentrated in a closed flask. The solution is then made alkaline to phenolphthalein and the colour discharged by one or two drops of 0·02*N*-sulphuric acid. Five drops of 10% potassium chromate solution are added and the chlorine is estimated in the usual way with 0·02*N*-silver nitrate solution.

G. W. R.

**Action of Potassium Ferrocyanide on Silver Haloids.** G. B. Bonino (*Gazzetta*, 1921, **51**, ii, 261—265).—Potassium ferrocyanide does not appear to interact with silver bromide or iodide

but with the chloride it reacts according to the equation: $3AgCl + K_4Fe(CN)_6 = Ag_3KFe(CN)_6 + 3KCl$. The chlorine ion may therefore be estimated in presence of the iodine ion by precipitating and washing the mixed silver haloids, treating the latter with a known volume of $0 \cdot 1N$-potassium ferrocyanide solution, removing the insoluble silver potassium ferrocyanide by filtration, and determining the amount of the residual potassium ferrocyanide by titration with standard permanganate solution. The reaction has not yet been studied quantitatively in presence of bromides.

T. H. P.

**Estimation of Small Quantities of Bromides and Chlorides in Iodides.** I. M. Kolthoff (*Pharm. Weekblad*, 1921, **58** 1568—1569).—The iodide in solution is treated with excess of sodium nitrite in presence of sulphuric acid. After filtering and boiling, to remove iodine and excess of nitrous acid, chlorides and bromides are estimated by Volhard's method. The method is quantitative, but does not distinguish between chlorides and bromides.

S. I. L.

**Bromine Normally Present in Animal Tissues.** A. Damiens (*Bull. Sci. Pharmacol.*, 1921, **28**, 85—93; from *Chem Zentr.*, 1921, iv, 847).—Thirty grams of finely-divided tissue are extracted by heating with dilute potassinm hydroxide solution. The dried residue is incinerated with a mixture of potassium nitrate and sodium carbonate, and the ash dissolved in water. Iodine is estimated in a portion of the solution as follows: the silver haloid precipitate, obtained by addition of silver nitrate solution in the presence of nitric acid, is suspended in water and a stream of chlorine is passed, first in the cold and then in the presence of 1 c.c. of sulphuric acid with warming. Air is passed through and the precipitate removed by centrifuging. The iodine is then estimated by a colorimetric method. Another portion of the solution is precipitated with silver nitrate and nitric acid. The precipitate is removed and the filtrate is treated with zinc and sulphuric acid. When less than a milligram of iodine is present bromine may be estimated colorimetrically in the filtrate. In the presence of larger amounts of iodine, the filtrate, after the reduction of the silver haloid precipitate, is neutralised with ammonia, diluted to 40 c.c. and after addition of 1 gram of iron ammonium sulphate, concentrated to 10 c.c. Bromine may then be estimated as before (cf. A., 1921, i, 476).

G. W. R.

**Estimation of Sulphur in Pyrites.** L. Gadaïs (*Ann. Chim Analyt.*, 1921, **3**, 330—335).—A critical review of Lunge's method and certain suggested modifications. For accurate work, the original method without alteration is to be preferred, care being taken to adhere strictly to all details of the operations. A variation of this method, in which the insoluble gangue is not filtered off before the precipitation of the iron with ammonia, is not recommended, as this gangue contains substances such as the sulphates of barium, strontium, calcium, and lead which may be partly

dissolved by ammonia and reprecipitated on subsequent acidification and addition of barium chloride. A second modification of Lunge's procedure, which obviates the washing of the gangue, consists in making up the solution in aqua regia to 100 c.c., filtering off 50 c.c., and proceeding with this aliquot portion as in the original method. This is free from serious objection provided the insoluble residue is comparatively small in amount. Finally, a rapid control method, not suitable for accurate work, consists in diluting the original solution to about 800 c.c., adding ammonia directly to this, digesting for two hours at a moderate temperature, cooling, making up the volume to 1000 c.c., and filtering off 500 c.c. in which sulphate is estimated in the usual way. G. F. M.

**Volumetric Estimation of Sulphide by Oxidation to Sulphate.** H. H. WILLARD and W. E. CAKE (*J. Amer. Chem. Soc.*, 1921, **43**, 1610—1614).—Sulphide is rapidly and quantitatively oxidised to sulphate by an excess of hypobromite in 2·5*N*-sodium hydroxide or by hypochlorite in 4*N*-sodium hydroxide. The excess of oxidising agent is determined iodometrically. The method gives accurate results for the estimation of sulphur in steels and in sulphides if care is taken to exclude all other reducing agents. In the case of steels, the method is used as follows: 5 grams of steel are placed in a flask, through which hydrogen may be passed, which is connected with a 10-bulb tube for absorbing the hydrogen sulphide. Air is removed from the apparatus by hydrogen and 100 c.c. of hydrochloric acid (*d* 1·1) are added. After the reaction has moderated, the solution is heated just to boiling for five minutes after the steel has dissolved. The solution in the absorption tube should contain 6—7 grams of sodium hydroxide in 50 c.c. of solution. The contents of the bulbs are washed with as little water as possible into a flask containing 10 c.c. of 0·3*N*-hypobromite solution and kept for three or four minutes, then 2 or 3 grams of potassium iodide are added, and the solution is diluted to 150 c.c. It is then exactly neutralised with concentrated hydrochloric acid and 5 c.c. excess added and titrated with 0·1*N*-sodium thiosulphate. If hypochlorite has been used instead of hypobromite, more sodium hydroxide must be used. Sulphides which are soluble in hydrochloric acid are estimated in the same way as steels. Insoluble sulphides are ignited with powdered iron in an atmosphere of hydrogen or carbon dioxide, thus prodncing ferrous sulphide. The estimation is then carried to completion as above. The error of the method is about 0·1%. J. F. S.

**Estimation of Sulphurous Acid.** VICTOR COPPETTI (*Ann. Chim. Analyt.*, 1921, **3**, 327—330).—The gravimetric method of Haas for the estimation of sulphurous acid, which consists in expelling the sulphur dioxide from the solution under examination by distillation in an atmosphere of carbon dioxide, absorbing the gas in a solution of iodine, and weighing the resulting sulphuric acid as barium sulphate, gives accurate results volumetrically if means are taken to prevent loss of iodine by volatilisation in the

current of carbon dioxide. For this purpose, an apparatus is described consisting essentially of a 300 c.c. flask to contain the iodine solution, to the bottom of which extends the gas delivery tube from the distillation flask. Surmounting the flask is a spherical absorption vessel containing $N/10$-thiosulphate solution, through which the carbon dioxide and iodine vapours leaving the flask must pass. When distillation is complete, the thiosulphate solution containing all the volatilised iodine is allowed to run back into the flask and the excess of iodine in the latter is titrated back with standard thiosulphate solution. G. F. M.

**The Estimation of Sulphates by means of a Suspension of Barium Chromate.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1921, **40**, 686—699; cf. Andrews, A., 1890, 414).—Although it would appear on theoretical grounds that an estimation of sulphate by means of barium chromate was not practicable, the method is valid, since the reaction $BaSO_4+CrO_4'' \rightleftharpoons BaCrO_4+SO_4''$ proceeds very slowly from left to right. The solution, acidified with hydrochloric acid, should be heated during neutralisation with ammonia to avoid the loss of chromic acid which accompanies the precipitation of barium chromate at ordinary temperatures, and, having regard to the hydrolysis of ammonium chromate, a slight excess of ammonia should be added. Barium chromate is adsorbed by ferric, aluminium, and zinc hydroxides, so that when these metals are present the method gives results which are too low, but trustworthy results can be obtained when ions which affect the reacting substances are absent. In presence of calcium, the results are too low, the error becoming smaller with increasing acidity of the solution and decreasing concentration of calcium. Practical details are given. H. J. E.

**Catalytic Action of Copper in the Oxidation of Ammonia by means of Persulphate.** G. SCAGLIARINI and G. TORELLI (*Gazzetta*, 1921, **51**, ii, 277—280).—Quantitative investigation of the oxidation of ammonia by means of either potassium or ammonium persulphate in presence of copper sulphate shows that the oxygen of the persulphate first oxidises the ammonia to nitrous acid, which is converted into ammonium nitrite, this being decomposed, with liberation of nitrogen, by the heat developed : $2NH_3+3O_2=2HNO_2+2H_2O$, $2NH_3+2HNO_2=2NH_4{\cdot}NO_2$, and $2NH_4{\cdot}NO_2=4H_2O+2N_2$. The catalytic effect of copper salts appears to be due to oxidation of the copper to a more highly oxidised compound, which passes on its surplus oxygen to the ammonia.

The estimation of persulphate by means of ferrous salts may be replaced advantageously by the following method, in which use is made of a Schultze and Tiemann's apparatus furnished with a mercury valve (*Z. anal. Chem.*, 1870, **9**, 401; *Ber.*, 1873, **6**, 1041) : 40 c.c. of water and 0·4—0·6 gram of copper sulphate are boiled in the flask for about ten minutes, the caoutchouc tube being then clipped and the boiling continued for five minutes to expel the air. The apparatus is allowed to cool, the mercury rising in

the barometer tube and a vacuum becoming established in the flask. A known volume of the persulphate solution and afterwards about 100 c.c. of ammonia solution are drawn into the cold flask through the clipped tube, the flask being then heated and the evolved gas collected over water and measured. The results obtained in this way agree exactly with those yielded by the ferrous sulphate method. T. H. P.

[**Method for the Estimation of Tri-, Tetra-, and Pentathionates present together in Solution with Sulphite, Thiosulphate, and Sulphate.**] E. H. RIESENFELD and G. W. FELD (*Z. anorg. Chem.*, **119**, 225—270). See this vol., ii, 45.

**The Accuracy of Dumas's Method for the Estimation of Nitrogen in the Cases of Substances rich in Nitrogen.** ERNST MOHR (*Ber.*, 1921, **54**, [*B*], 2758—2767).—A mathematical treatment of the influence of the errors in measuring weight of substance, volume of nitrogen, temperature and pressure on the accuracy of the process.

The usual procedure of estimating the volume accurately to within 0·05 or 0·1 c.c., and the temperature and pressure to degrees Centigrade and millimetres of mercury is sufficient for substances containing 20—25% of nitrogen, but involves considerable error when more than this amount is present. The errors due to inaccurate reading of pressure and temperature cannot be minimised by increasing the weight of substance taken. On the other hand, the errors due to volume and weight of substance become considerable when a small quantity of substance is taken and can be diminished by increasing the amount. The practice of using small weights of material when dealing with substances rich in nitrogen by Dumas's method is to be deprecated; Pregl's method should be used in preference. The error involved in the measurement of pressure does not depend to an appreciable extent on whether the gas is moist or dry (above 50% potassium hydroxide solution), but the error involved in measurement of temperature is lower in the latter case. In spite of this fact, the measurement is generally made in preference over water by reason of the customary large diameter of the Schiff's nitrometer and the formation of foam over the potassium hydroxide solution.

A simple and accurate method of calculation is as follows. The temperature is first brought to whole degrees by addition or subtraction of $x^\circ$ in the direction of smallest change and the pressure is then changed by $3x$ mm. in the same sense as the alteration of temperature.

A plea is entered for the more uniform recording of analytical data in the literature and more precise statement of the exact condition of the nitrogen with respect to moisture as also for the reduction of pressures to 0°. H. W.

**The Kjeldahl Nitrogen Method and its Modifications.** A. E. PAUL and E. H. BERRY (*J. Assoc. Off. Agric. Chem.*, 1921, **5**, 108—132).—Investigations are described into the most suitable

apparatus and method for the nitrogen estimation, with particular reference to the case of cotton-seed meal as presenting special difficulty. The most suitable type of bulb-trap for use in the distillation is the one in which both inlet and outlet tubes enter the bulb and are bent in opposite directions. It is advisable, although not absolutely necessary, to have enough acid in the receiver to neutralise all the ammonia distilled. Practically all the ammonia appears in the first 75 c.c. of the distillate, and all is in the first 100 c.c. During the initial digestion of the material with acid, the flame should never touch the flask above the surface of the liquid; the flask should be protected by a ring of asbestos. The volume of the digesting liquid should at no time be less than 10 c.c. If mercury is used to aid the digestion there is a loss of from 2 to 15% of ammonia unless enough potassium sulphide is added to precipitate all the mercury before distillation. The use of copper sulphate during digestion does not necessitate the subsequent addition of potassium sulphide. The use of permanganate is unnecessary. Digestion with sulphuric acid alone never gives maximum results. Mercury gives a much more rapid digestion than copper salts, and potassium sulphate is more efficient than sodium sulphate. The most rapid and efficient digestion is given by the use of 0·7 gram of mercuric oxide and 10 grams of potassium sulphate. In this way, the liquid becomes clear in one to one and a half hours and further heating for three hours completes the digestion. The amount of copper used in the digestion has little effect on the result. A 2 gram sample of cotton-seed meal and similar substances is preferable. Digestion should not be carried out in an atmosphere containing nitrous fumes. Nitrates in the digestion mixture are not only entirely lost, but they also bring about a considerable reduction in the amount of ammonia recovered. A. G. P.

**Modification in the Kossel-Neumann Method for the Estimation of Phosphorus in Organic Substances.** MARIO A. MANCINI (*Biochem. ter. sper.*, 1921, **8**, 4—7; cf. Falk and Sugiura, A., 1915, ii, 577).—0·5 Gram of the substance is heated in a 200 c.c. Kjeldahl flask with 6—8 c.c. of sulphuric acid (*d* 1·184), the boiling being continued for one hour. Nitric acid (*d* 1·4) having been carefully added drop by drop, boiling is continued until the evolution of oxides of nitrogen ceases. The operation is repeated four or five times. The clear, light yellow liquid is washed into a beaker with hot water, and ammonium hydroxide solution is added in slight excess, followed by 30—40 c.c. of 40% ammonium nitrate solution and 20 c.c. of 25% nitric acid. The liquid is mixed, at 100°, with 120—140 c.c. of a boiling 3% solution of ammonium molybdate. After being kept for at least two hours it is filtered and the precipitate washed with a hot solution containing 50 c.c. of nitric acid and 50 grams of ammonium nitrate per litre. Hot 25% ammonium hydroxide solution is poured over the filter, which is washed with hot water until the washings give no reaction with Nessler's reagent. To the filtrate is added

50 c.c. of ammoniacal "magnesia mixture," and, after being kept for twenty-four hours, the precipitate is filtered, washed, and ignited in the usual manner. CHEMICAL ABSTRACTS.

**The Composition and Preparation of a Neutral Solution of Ammonium Citrate.** C. S. ROBINSON (*J. Assoc. Off. Agric. Chem.*, 1921, **5**, 93—97).—To overcome the confusion attached to the term "neutral ammonium citrate solution," it is recommended that such a solution should be one showing a $p_H$ value of 7·0. The solution contains 45·33 grams of ammonia and 172·00 grams of anhydrous citric acid per litre at 20° and has *d* 1·09. To prepare a litre of solution 172·00 grams of anhydrous citric acid are dissolved in 700 c.c. of water, nearly neutralised, cooled, and made up to a convenient volume, maintaining the density above 1·09. Of this, 5 c.c. are diluted to about 20 c.c., and standard ammonia solution is added until the colour produced with pheuol-red indicator matches that produced with the same quantity of indicator by an equal volume of neutral standard phosphate solution (50 c.c. of *M*/5-dihydrogen potassium phosphate +29·63 c.c. of *M*/5 sodium hydroxide in 200 c.c.). The calculated amount of ammonia is then added to the bulk of the solution.

A. G. P.

**A Modified Method for the Estimation of Phosphoric Acid.** A. W. CLARK and R. F. KEELER (*J. Assoc. Off. Agric. Chem.*, 1921, **5**, 103—105).—Two grams of the sample are dissolved in 30 c.c. of concentrated nitric acid and 10 c.c. of hydrochloric acid. The solution is diluted to 200 c.c. and filtered through a dry filter. A portion equivalent to about 0·25 gram is neutralised with ammonia and acidified with nitric acid. Fifty c.c. of 20% ammonium nitrate solution are added and then sufficient ammonium molybdate solution. After remaining over-night, the precipitate is collected on a Gooch crucible, washed eight times with 2% nitric acid (12—13 c.c. each time), then twice with cold water, and dried for two hours at 120°. Precipitation in the cold and drying at 120° give a less variable precipitate than the usual method. The conversion factor of ammonium phosphomolybdate to phosphoric acid is 0·03723. A. G. P.

**Nephelometric Method for the Estimation of Phosphoric Acid and its Compounds in Small Quantities of Blood.** W. R. BLOOR (*Bull. Soc. Chim. Biol.*, 1921, **3**, 451—475).—A detailed description of the author's adaptation (A., 1918, ii, 452) of Kober and Egerer's method (A., 1915, ii, 794). E. S.

**Toxicology of Arsenic.** N. TARUGI (*Boll. Chim. Farm.*, 1921, **60**, 569—576).—The results of experiments with rabbits and guinea-pigs show that arsenic, either organically combined or mixed mechanically with organic matter, always yields gases containing arsenic when putrefaction occurs. Such evolution of gas may occur quickly and must be borne in mind in cases of suspected arsenical poisoning. In the putrefaction of animal matter, the mechanism by which gaseous arsenic compounds are formed

is more complicated than the action of the "arsenic moulds," since such gases are not formed in the initial stages of the putrefaction where aerobiosis appears to predominate, and since also the gases contain not only alkylarsines but hydrogen arsenide as well. T. H. P.

**The Use of Silica Crucibles for the Estimation of Potassium in Soils.** J. S. Jones and J. C. Reeder (*Soil Sci.*, 1921, **12**, 419—432).—For the estimation of potassium in soils by the fusion method, silica crucibles may be used instead of platinum, provided that certain limits of temperature are observed. To ensure perfect fusion, the muffle must reach a temperature of 812°, and to avoid loss of potassium by volatilisation the temperature must not exceed 855°. For this purpose an electrically heated muffle is preferable. An electrical arrangement for heating a silica crucible of the J. L. Smith type, 10 cm. long, 2 cm. in diameter at the top, and 1·8 cm. at the bottom is described and is very satisfactory for this type of work. W. G.

**Detection of Magnesium in Presence of Manganese and Phosphoric Acid.** A. Purgotti (*Gazzetta*, 1921, **51**, ii, 265—266).—In presence of phosphoric acid, manganese is precipitated almost completely as tertiary manganous phosphate, even from solutions containing large proportions of ammonium chloride; the precipitate undergoes gradual or, in the hot, rapid transformation into pale pink crystals of manganous ammonium phosphate, analogous in composition and properties to magnesium ammonium phosphate. The formation of this manganese precipitate and hence the danger of mistaking it for the magnesium precipitate may be avoided by treating the hydrochloric acid solution, not only with ammonia solution to remove the kations accompanying magnesium, but also at the same time with ammonium sulphide, which eliminates the whole of the manganese as sulphide; the filtrate is then tested for magnesium.

If the metals of the third group are precipitated in the usual way with ammonia solution, manganese phosphate is precipitated in considerable quantity in addition to certain amounts of calcium, barium, and strontium phosphates, a little manganese and much calcium, barium, and strontium passing into solution. Similar behaviour is shown by a mixture of magnesium phosphate with a manganese salt, but less magnesium goes into solution and still less manganese is precipitated as phosphate. If the quantity of manganese salt is very considerably greater than that of the calcium, barium, and strontium phosphates, the equilibrium, $Ca_3(PO_4)_2 + 3Mn(OH)_2 \rightleftharpoons Mn_3(PO_4)_2 + 3Ca(OH)_2$, is displaced towards the right hand side and the calcium, barium, and strontium pass into solution almost completely. T. H. P.

**Apparatus for the Gasometric Estimation of Zinc in Zinc Powder.** Edgar Beyne (*Ann. Chim. Analyt.*, 1921, **3**, 360).—The apparatus consists of a gas burette, the upper part of which below the glass stop-cock is expanded into a bulb of 300 c.c.

capacity, and the lower part is graduated in 0·5 c.c. from 300 c.c. to 375 c.c. The lower end of the burette is connected with a rubber tube to a bulb for adjusting the liquid level and gas pressure in the burette, and the upper end is connected through a small refrigerating spiral to a Koninck apparatus which is charged with the zinc dust under examination, and a mineral acid. In a simpler form of apparatus the latter is replaced by an ordinary flask connected by means of a glass tube with the stop-cock of the burette.

G. F. M.

**The Direct Iodometric Estimation of Lead Peroxide.** Samuel Glasstone (T., 1921, **119**, 1997—2001).

**A Very Sensitive Reagent for Copper: the Kastle-Meyer Reagent.** Pierre Thomas and Georges Carpentier (*Compt. rend.*, 1921, **173**, 1082—1085).—The Kastle-Meyer reagent, which is a 2% solution of phenolphthalein in 20% potassium hydroxide solution decolorised by boiling with zinc powder, gives a pink coloration witb copper salts and is capable of detecting 1 part of copper in 100,000,000 parts of water. Four drops of the reagent are added to 10 c.c. of the solution to be tested and then one drop of hydrogen peroxide (5—6 vols.). W. G.

**The Iodometric Estimation of Copper and Arsenic present together, especially in Paris and Schweinfürth Green.** I. M. Kolthoff and C. J. Cremer (*Pharm. Weekblad*, 1921, **58**, 1620—1624).—Arsenic trioxide can be estimated by means of iodine if the cupric-ion concentration is very much reduced, which can be effected hy addition of excess of pyrophosphate or tartrate, with which the copper forms complex salts. 0·6—0·8 Gram of the pigment is boiled with 25 c.c. of water and 5 grams of sodium pyrophosphate to a clear solution. After cooling, *N*/10-iodine solution is added until the deep blue solution becomes green; the end-point is very sharp. The iodine required is equivalent to the arsenious oxide present. Ten c.c. of 4*N*-sulphuric acid and 2 grams of potassium iodide are then added, and after ten minutes the iodine liberated by reduction of the cupric compound is titrated with *N*/10-thiosulphate, starch being added towards the end.

The results were checked by analysis of the pigments by the standard Lunge-Berl method. This method was found unsatisfactory for copper, the results being always high. Addition of hydrazine sulphate before the sodium hydroxide reduces the copper compound, the element being precipitated and weighed as metal; this modification is much more accurate than the accepted method.

The iodine titration is rapid and simple, and gives accurate results for both elements. S. I. L.

**Separation and Estimation of Copper, Lead, Antimony, and Tin. Analysis of White Metals.** A. Kling and A. Lassieur (*Compt. rend.*, 1921, **173**, 1081—1082).—0·5—1·0 Gram of the alloy is dissolved in 10 c.c. of hydrochloric acid in the presence of potassium chlorate. The solution is diluted to 100 c.c.,

and neutralised with sodium hydroxide. Any precipitate formed is redissolved by the addition of 4—5 grams of tartaric acid. The liquid is transferred to a conical flask coated inside with wax, and to it are added 10 c.c. of concentrated hydrofluoric acid and then, after half an hour, 10 grams of sodium acetate, 1 c.c. of glacial acetic acid and water to bring the volume to 300 c.c. A white precipitate of lead fluoride is formed, but to the liquid 20 c.c. of a 10% solution of sodium sulphide are added and after a time the precipitate of the sulphides of copper, lead, and antimony is filtered off. In the filtrate the tin may be estimated either by precipitation with cupferron (cf. A., 1920, ii, 452), or electrolytically after decomposition of the complex fluoro-compound by the addition of boric acid and redissolving the tin sulphide by boiling with hydrogen peroxide. The precipitate of the mixed sulphides is extracted with 80 c.c. of sodium sulphide solution (*d* 1·14) and the antimony estimated electrolytically in the extract after the addition of potassium cyanide. The copper and lead sulphides are dissolved in nitric acid and the two metals estimated simultaneously by electrolysis. W. G.

**Estimation of Mercury in the Mercurial Pills of the [French] Codex.** MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1921, **24**, 369—379; *Ann. Falsif.*, 1921, **14**, 340—347).—The pills are heated with concentrated nitric acid for two hours on a water-bath, and after a further two hours the solution is filtered, and the destruction of the organic matter is completed by adding a small quantity of a 10% solution of bromine. After ten minutes the liquid is rendered strongly alkaline with sodium hydroxide and after adding potassium iodide the mercury is precipitated in the form of a grey powder by means of formaldehyde solution. After two hours the supernatant liquid is decanted through a filter, the mercury is washed with dilute sodium hydroxide solution, and is then treated, together with the filter-paper and its contents, with diluted acetic acid and *N*/10-iodine solution. After ten minutes' agitation, the mercury is completely transformed into mercuric iodide, which dissolves in the potassium iodide present, and the excess of iodine is titrated back with thiosulphate. The method is of general application to all the mercurial pills of the French Codex without modification except in the case of opiated mercurous iodide pills, with which, after treatment with nitric acid, a crystalline precipitate of mercuric iodonitrate, $HgI_2,Hg(NO_3)_2$, is formed. All that is necessary in this case, however, is to dissolve the crystals in the liquor by addition of potassium iodide, and omitting the bromine treatment, to proceed with the precipitation of the mercury as above. In pills containing soap, although the fat acids are not destroyed by the nitric acid treatment, they do not retain any mercury in combination, and form a layer on the surface of the liquor, which solidifies on cooling, and is therefore easily separated. G. F. M.

**Volumetric Estimation of Aluminium.** ERNST JOSEF KRAUS (*Chem. Zeit.*, 1921, **45**, 1173).—The neutral or faintly acid solution containing the aluminium in the form of sulphate, and free from

other interfering metals, is titrated with standard disodium hydrogen phosphate solution, a few drops of silver nitrate solution being used as indicator, as yellow silver phosphate only commences to form after all the aluminium has been precipitated as phosphate according to the equation: $Al_2(SO_4)_3+2Na_2HPO_4=2AlPO_4+2Na_2SO_4+H_2SO_4$. The titration is preferably carried out in a boiling solution as the silver phosphate is more pronouncedly yellow in colour and therefore more easily noticeable under these conditions. In presence of other metals, such as iron, etc., the aluminium should first be separated, by addition of excess of sodium hydroxide, for example, and finally precipitated as hydroxide with ammonia. The precipitate after washing is dissolved in a slight excess of dilute sulphuric acid to form a solution suitable for the titration. The method gives good results even when only very small quantities of the metal are to be estimated. G. F. M.

**Improved Method for the Separation of Iron and Manganese.** M. CARUS (*Chem. Zeit.*, 1921, **45**, 1194).—In the usual method for the separation of manganese from the metals of the iron group by precipitating the latter as basic acetates, the contamination of the precipitate with manganese is not due to the co-precipitation of the basic acetate of this metal, but to the formation of insoluble higher oxidation products owing to the action of dissolved oxygen. A perfect separation of the manganese in one operation, even when a large excess is present, is obtained by causing the precipitation with sodium acetate to occur in presence of a small quantity of hydrogen peroxide, in which case no oxidation of the manganese salts can occur. The precipitate obtained, after washing with dilute acetic acid containing a small quantity of sodium acetate and hydrogen peroxide, and finally with hot water, is then completely free from manganese. G. F. M.

**The Acidimetric Estimation of Dichromate.** I. M. KOLTHOFF and E. H. VOGELENZANG (*Rec. trav. chim.*, 1921, **40**, 681—685).—By reason of the hydrolysis of potassium chromate solution, neither chromic acid nor dichromate can be neutralised using phenolphthalein as indicator. A study of the neutralisation of dichromate with sodium hydroxide leads to the following conclusions:—Thymolphthalein should be used as indicator; if phenolphthalein is used the solution must have been saturated previously with sodium chloride, or barium chloride must be used to precipitate the chromate formed. The barium chloride may only be added when the solution is already yellow, otherwise the precipitate of barium chromate contains chromic acid. It is claimed that the results are correct to within 0·2%, but the method is not recommended owing to difficulties with the indicator.

H. J. E.

**Modified Method for the Estimation of Iron and Vanadium after Reduction by Hydrogen Sulphide.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1921, **43**, 1560—1568).—The estimation of iron or of vanadium by reduction with

hydrogen sulphide followed by titration with potassium permanganate or dichromate ordinarily leads to high values. These high values are not due to the presence of sulphur, and persist in spite of the complete expulsion of hydrogen sulphide and the avoidance of organic matter extracted from filter-paper. They may be ascribed to polythionic acids which are not destroyed by boiling in moderately concentrated sulphuric acid solution and are volatilised slowly from dilute and more rapidly from concentrated solutions. Reasonably accurate estimations may be made by restricting the volume of the original solution to 100 c.c. and proceeding by the following modified process. The solution is acidified with sulphuric acid until it contains 2·5% sulphuric acid by volume, reduced by hydrogen sulphide for thirty minutes in cold solution, and for a further fifteen minutes, during which the solution is raised to the boiling point. The hot solution is treated with 15 c.c. of 1 : 1-sulphuric acid and boiled for thirty to sixty minutes, during which a stream of carbon dioxide is passed through, until the total volume of liquid is about 50 c.c. The solution is cooled, the current of carbon dioxide being maintained, diluted to 200 c.c., and titrated with standard permanganate solution. In some cases it is advisahle to filter off the separated sulphur after the hydrogen sulphide treatment. The filtrate is treated for a further ten minutes with hydrogen sulphide and the process completed as above. The average errors found by this method are for iron 0·5% and for vanadium 0·1%. For accurate estimations of iron and vanadium in solutions containing platinum (as in rock analysis), a preliminary separation of the hydrogen sulphide group, followed by expulsion of the gas, complete oxidation with permanganate, and reduction with sulphur dioxide is recommended. J. F. S.

**Estimation of Vanadium and Chromium in Ferrovanadium by Electrometric Titration.** G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright (*J. Ind. Eng. Chem.*, 1921, **13**, 939—941).—Three grams of the ferrovanadium are dissolved in a mixture of nitric acid and hydrochloric acid, sulphuric acid is then added, the mixture evaporated to expel all nitric acid and hydrochloric acid, cooled, and the solution diluted to 1000 c.c. One hundred c.c. of this solution are treated with 25 c.c. of sulphuric acid (*d* 1·58), diluted to 300 c.c., boiled, and 20 c.c. of 10% ammonium persulphate solution and 10 c.c. of 0·25% silver nitrate solution are added; the mixture is boiled for ten minutes, 5 c.c. of hydrochloric acid (1 : 3), are then added, the boiling is continued for a further ten minutes, the mixture treated with 26 c.c. of sulphuric acid, cooled at 5°, and titrated with ferrous ammonium sulphate solution, the end-point of the titration being determined electrometrically. This titration is a measure of the vanadium and chromium together. The vanadium is estimated by boiling 100 c.c. of the original solution with a few c.c. of ferrous sulphate solution, adding 20 c.c. of sulphuric acid, *d* 1·58, and 40 c.c. of nitric acid (*d* 1·40), diluting the mixture to 200 c.c., and boiling it at such a rate that the volume is reduced to 100 c.c. in one hour.

The solutiou is then cooled and titrated as before. The differenc between the two titrations is a measure of the amount of chromiun present. W. P. S.

**[Estimation of Antimony as Sodium Antimonate.]** E. S TOMULA (*Z. anorg. Chem.*, 1921, **118**, 81—92).—See this vol., ii, 74

**Estimation of Bismuth.** O. A. CRITCHETT (*Eng. and Min. J* 1921, **112**, 58).—A solution of the ore in a mixture of nitric an hydrochloric acids, having been evaporated with sulphuric aci until fumes appear, is diluted, treated with a drop of hydrochlori acid, filtered, and the filtrate boiled with sodium thiosulphat and aluminium foil. The precipitate is collected, returned to th beaker with hot water, potassium hydroxide added, and the liquic after having been boiled, is filtered through the original pape The latter, with the precipitate, is repeatedly evaporated wit nitric and sulphuric acids until the paper is completely destroyec After dilution, boiling, filtering, addition of a slight excess c ammonium hydroxide, and again boiling, the precipitate is collectec washed, and dissolved in hot dilute nitric acid. The bismuth ma then be estimated (*a*) as oxide after treatment with ammoniur carbonate, (*b*) as oxychloride after neutralising with ammoniur hydroxide, adding a little hydrochloric acid, diluting, and boiling or (*c*) by titration with permanganate after dilution, treatmen with ammonium oxalate, boiling, and separation, with subsequen washing by decantation with hot water, of the precipitate o bismuth oxalate. CHEMICAL ABSTRACTS.

**Analytical Chemistry of Tantalum, Columbium, and thei Mineral Associates. I. The Use of Tartaric Acid in th Analysis of Natural Tantalocolumbates. II. The Separa tion of Zirconium from Tantalum and from Columbium** WALTER RAYMOND SCHOELLER and ALAN RICHARD POWEL (T., 1921, **119**, 1927—1935).

**Evaluation of the Degree of Unsaturation of Mineral Oil in the Bergius Process.** H. I. WATERMAN and J. N. J. PERQUI (*Rec. trav. chim.*, 1921, **40**, 677—680; cf. Dean and Hill, Technica Paper 181, *Bureau of Mines*, 1917).—Determination of the iodin number of an unrefined mineral oil, before and after treatmen by the Bergius process, shows that it is a little greater afte treatment. H. J. E.

**Estimation of Phenanthrene.** ARTHUR G. WILLIAMS (*J Amer. Chem. Soc.*, 1921, **43**, 1911—1919).—The phenanthrene i oxidised by iodic acid to phenanthraquinone, which is precipitate as toluphenanthrazine by means of 3 : 4-tolylenediamine an weighed as such, the procedure being as follows:

For materials containing 30% or more of phenanthrene, 0·25 gran is weighed into a 50 c.c. conical flask, 0·75 gram of iodic acid an 20 c.c. of glacial acetic acid are added and the mixture is boile for two and a half hours under an air condenser. After cooling fo

several hours, any anthraquinone formed from anthracene present in the original material is filtered off on a Gooch crucible and washed with the minimum amount of glacial acetic acid. The filtrate and washings are evaporated to slightly less than 25 c.c. and then the volume is made exactly to 25 c.c., the mixture is cooled and 1 gram of 3 : 4-tolylenediamine is added and the flask left in running water at 20° over-night. The toluphenanthrazine is collected in a Gooch crucible and washed first with 25 c.c. of 50% acetic acid saturated with the phenanthrazine and then with 200 c.c. of cold water. The precipitate is dried and weighed and to the weight is added 0·053 gram to allow for the toluphenanthrazine remaining in solution in the 25 c.c. of glacial acetic acid. The factor for conversion into phenanthrene is 0·6052. Carbazole, if present in amounts exceeding 10%, interferes in the determination of phenanthrene, and some of the high-boiling coal tar constituents interfere; a crude anthracene cannot be directly analysed.

For the detection of phenanthrene, the material is oxidised as described above, the mixture being cooled and filtered. The filtrate is poured into water and the precipitate collected and washed with water. The precipitate is warmed with concentrated sodium hydrogen sulphite solution and any residue is filtered off. The filtrate is washed in a separating funnel with one or two portions of carbon tetrachloride and then, after the addition of a fresh portion of carbon tetrachloride, is acidified with hydrochloric acid containing ferric chloride. The carbon tetrachloride layer, which contains the phenanthraquinone, is separated and tested by Hilpert and Wolf's reaction (cf. A., 1913, ii, 733), using a solution of antimony pentachloride in carbon tetrachloride, a purplish-red precipitate being obtained on boiling if phenanthrene was originally present. W. G.

**Chemical Analysis of Caoutchouc Articles.** ANDRÉ DUBOSC (*Ann. Chim. Analyt.*, 1921, **3**, 335—344).—A résumé of the methods employed and the estimations necessary for a complete chemical analysis of caoutchouc and ebonite articles. (1) The acetone extract contains the natural resins, added resins, free sulphur, oils, and waxes, and is evaporated to dryness and quantitatively examined for these substances by the usual methods. (2) The chloroform extract should be almost colourless. Brown coloration indicates the presence of tar or asphaltic adulterants. (3) The extract in alcoholic potash of the insoluble residue of the chloroform extraction should not exceed 15% from a material containing about 50% of caoutchouc, a larger proportion indicating added oils or fats. (4) The aqueous extract reveals the presence of starch or dextrins. (5) The estimation of total sulphur is best carried out by Henriquez's method as modified by the Bureau of Standards. (6) The ash is determined on the residue from the acetone extraction, and a rough estimate of the caoutchouc content can be obtained by subtracting ash and total sulphur from 100. (7) None of the various methods which have been proposed for the estimation of caoutchouc itself give entire satisfaction. The

total foreign matter may be obtained, however, by solution in boiling nitrobenzene, diluting with chloroform, filtering through a tared filter, washing with acetone, drying, and weighing. G. F. M.

**Estimation of Oxalic Acid in Urine.** E. SALKOWSKI (*Biochem. Z.*, 1921, **118**, 259—266).—A reply to Bau's criticism of the author's method (A., 1921, ii, 356). H. K.

**Estimation of the Amino-acids of Feeding Stuffs.** T. S. HAMILTON, W. B. NEVENS, and H. S. GRINDLEY (*J. Biol. Chem.*, 1921, **48**, 249—272).—Further improvements are made in the application of Van Slyke's method to the estimation of amino-acids in feeding stuffs (cf. Eckstein and Grindley, A., 1919, ii, 204). Non-protein nitrogen is first removed from the material by successive extractions with anhydrous ether, cold absolute alcohol, and cold 1% trichloroacetic acid, any protein removed by the latter being recovered by precipitation with colloidal ferric hydroxide. The main portion of the protein is then extracted with dilute (0·2%) sodium hydroxide. Starch is removed from the residue by treatment with hot 2% trichloroacetic acid and the remaining protein extracted by treatment first with boiling 20% hydrochloric acid and then with cold 5% sodium hydroxide. A small quantity of protein extracted with the starch is recovered by precipitation of the latter by addition of alcohol. The various fractions of protein thus obtained are hydrolysed with concentrated hydrochloric acid, united, and submitted to the Van Slyke analysis. The method is applied to oats, corn, cotton-seed meal, and lucerne. E. S.

**Estimation of Hippuric Acid in Urine.** J. SNAPPER and E. LAQUEUR (*Arch. Néerl. Physiol.*, 1921, **6**, 48—57).—To 100 c.c. of urine 25 grams of sodium chloride are added, and a little concentrated hydrochloric acid. An aliquot portion is extracted six times with ethyl acetate, and the total extract is washed once with one-quarter of its volume of water. The wash water is washed with an equal volume of ethyl acetate, which is added to the original extract. After evaporation of the ethyl acetate, the urea is decomposed by sodium hypobromite, and the residual hippuric acid estimated by Kjeldahl's method. G. B.

**The Rotation of Dextrose in Solutions of Trisodium Phosphate. Mutarotation as an Analytical Method.** HANS MURSCHHAUSER (*Biochem. Z.*, 1921, **117**, 215—225).—The mutarotation of dextrose is accelerated by trisodium phosphate. It follows a unimolecular law, the velocity constants being also linear functions of the concentration of sodium phosphate. As the mutarotation is a function of the hydroxyl ion, its use is indicated for distinguishing salts of different alkalinity. H. K.

**Conditions Affecting the Quantitative Estimation of Reducing Sugars by Fehling's Solution. Elimination of certain Errors Involved in Current Methods.** F. A. QUISUMBING and A. W. THOMAS (*J. Amer. Chem. Soc.*, 1921, **43**, 1503—1526).—The various sources of error in the current methods of

using Fehling's solution are discussed. The inter-relationship of temperature, 60—110°, and time of heating, ten minutes to two hours, to determine the best time and optimum temperature for reduction has been investigated. Fehling's solution has been studied from the point of view of the nature and concentration of the alkali, concentration of copper sulphate and potassium sodium tartrate, to find the maximum and minimum concentrations of these constituents necessary to give the greatest yield of cuprous oxide and to ensure the formation of the complex cupric tartrate ion. Auto-reduction of Fehling's solution at different times and temperatures of heating has been measured, showing those conditions under which absolutely no "blank" reduction is obtained. Conditions affecting the physical properties of the precipitated cuprous oxide, the photosensitiveness, and the keeping quality of Fehling's solution are recorded. A study of surface oxidation involving different methods of heating and vessels of various sizes has been carried out in order to determine the loss of copper due to surface oxidation and how to avoid it. The catalytic effect of the walls of the container has been demonstrated. A modified method of procedure for the estimation of sugars by means of Fehling's solution is described. In this method the solutions required are, (1) copper sulphate solution containing 82·4 grams of $CuSO_4,5H_2O$ per litre, (2) alkaline tartrate solution; 376 grams of crystallised potassium sodium tartrate dissolved in water in a litre flask, and the calculated amount of sodium hydroxide solution added to make 1 litre of this solution containing 130 grams of sodium hydroxide. The sodium hydroxide is made from material purified by alcohol which is kept in concentrated solution for several days to allow carbonates and other insoluble impurities to separate. To make an estimation, 25 c.c. of the copper sulphate solution, 25 c.c. of the alkaline tartrate solution, and 50 c.c. of the sugar solution are placed in a beaker and warmed on a water-bath at 80°. After exactly thirty minutes, the cuprous oxide is filtered on a Gooch crucible and washed. This may either be dried and weighed as cuprous oxide, or dissolved in nitric acid and estimated electrolytically. From the weight of copper, the amount of sugar may be obtained from tables which are given in the paper or by means of the following equations, in which $x$ is the amount in milligrams of copper obtained from $y$ mg. of sugar: dextrose, $y=0·474x+0·000115x^2$; lævulose, $y=0·526x+0·000078x^2$; lactose, $y=0·813x+0·000003x^2$; maltose, $y=0·990x+0·0000005x^2$; and invert-sugar, $y=0·504x+0·0000870x^2$. This method is designed for use in the analysis of saccharine materials containing sucrose, dextrose, lævulose, invert-sugar, lactose, and maltose. It is not claimed that the method can be used for the accurate quantitative estimation of 0·1% or less of invert-sugar in approximately pure sucrose. J. F. S.

**Errors in the Estimation of Sugar by Fermentation with Yeast.** CARL LANGE (*Berlin Klin. Woch.*, 1921, **58**, 957—959; from *Chem. Zentr.*, 1921, iv, 848).—The estimation of sugar in

urine by fermentation with yeast is subject to certain errors. The evolved gas is not entirely carbon dioxide, but contains also nitrogen from the reaction of carbamide, ammonia, or amino-acids with nitrites. The latter may be formed by reduction of nitrates in the urine, or may occur in the yeast. There may also be an evolution of carbon dioxide from carbonates present in the urine. Errors may be diminished to some extent by sterilisation, and precipitation of carbonates with calcium chloride. The estimation of sugar in urine, however, gives only an approximate value.
G. W. R.

**Limitations of the Modified Lewis-Benedict Method of Blood Sugar Estimation.** RUTH A. GUY (*Biochem. J.*, 1921, **15**, 575—576).—0·0001 Gram of acetone added to 2 c.c. of blood produces an observable colour change in Lewis and Benedict's picric acid method of sugar estimation (A., 1915, ii, 111), but no change is noted with similar quantities of acetoacetic acid. G. B.

**The Catalytic Power of Flour.** O. FERNÁNDEZ and A. PIZARROSO (*Anal. Fis. Quím.*, 1921, **19**, 265—268).—The catalytic activity of flour, measured by its decomposition of hydrogen peroxide, has been proposed as a measure of its grade of extraction. The results obtained by the authors, using samples of flour of different origin, showed no correlation between catalytic activity and total- or phytin-phosphorus. The test is held to be of little value.
G. W. R.

**Identification of Oxycellulose by means of the Barium Compound.** ERNST BECKER (*Zellstoff u. Papier*, 1921, **1**, 5—7).—When 2 grams of oxycellulose are shaken with 50—60 c.c. of barium hydroxide solution for four hours, and the insoluble portion is washed with water until the filtrate is free from barium compounds, a barium compound of oxycellulose remains, of which the content of barium varies according to the origin of the oxycellulose.
CHEMICAL ABSTRACTS.

**Benzidine Hydrochloride as a Reagent for Wood Cells.** C. VAN ZIJP (*Pharm. Weekblad*, 1921, **58**, 1539—1542).—A solution of 0·2 gram of benzidine in 19 c.c. of water, to which 1 c.c. of 25% hydrochloric acid has been added, gives an orange stain to ligneous matter in microscope sections. Sections of material containing tannins or acids which act on iron should be washed free from iron with a 1% solution of hydrochloric acid in alcohol after cutting. Starch can be stained with iodine in the same section without interfering. The reagent also detects diseased tissues in Hevea bark, and for this reason, as well as because of its cheapness as compared with phloroglucinol, is of great use for control on rubber plantations.
S. I. L.

**Detection of Formaldehyde with Phenols.** B. PFYL, G. REIF, and A. HANNER (*Chem. Zeit.*, 1921, **45**, 1220—1221).—Phenol reactions for the detection of formaldehyde as previously carried out (cf. A., 1921, ii, 663) are not sufficiently trustworthy

when the test is to be adapted to the detection of methyl alcohol in potable spirits and tinctures after distillation with permanganate, as colour reactions are often simultaneously given by the traces of other aldehydes, alcohols, etc., which pass over into the distillate, and the mixed colours produced allow of no certain conclusions being drawn. A solution of guaiacol, or of *apo*morphine hydrochloride in concentrated sulphuric acid (0·02 gram in 10 c.c.) gives, however, a reagent with which a sharp distinction can always be observed if methyl alcohol is present in the original tincture. The reaction is best carried out by adding a few drops of the distillate to 0·5 c.c. of the reagent in a watch glass. With the guaiacol reagent a clear dark red colour is produced when formaldehyde is present which is readily distinguished from the pale yellow coloration produced in its absence, whilst with the *apo*morphine reagent a characteristic precipitate is formed in presence of formaldehyde. As little as 0·25% of methyl alcohol in tinctures, etc., can be detected with certainty by the new method. G. F. M.

**Orcinol Reaction of Furfuraldehyde.** ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1921, [vii], **24**, 334—336).—As little as 1 part of furfuraldehyde in 600,000 parts of solution may be detected by the blue coloration which is obtained when 5 c.c. of the solution, 5 c.c. of hydrochloric acid, and 0·02 gram of orcinol are heated together, cooled, and shaken with a few drops of amyl alcohol.
W. P. S.

**Source of Error in Tests for Acetone.** E. PITTARELLI (*Policlinico*, 1921, **28**, 621; *J. Am. Med. Assoc.*, **76**, 1803).—Caoutchouc under the influence of steam or boiling water yields a volatile substance which responds to all the tests most characteristic of acetone; therefore conclusions based on technique involving distillation in the presence of caoutchouc may be misleading.
CHEMICAL ABSTRACTS.

**Microchemical Reactions of "Dulcin" [*p*-Ethoxyphenylcarbamide].** G. DENIGÈS and R. TOURROU (*Compt. rend.*, 1921, **173**, 1184—1186).—When a few particles of "dulcin" on a microscope slide are moistened with one drop of nitric acid (*d* 1·39) they dissolve and on the addition of a drop of water microscopic orange or brick-red crystals of *p*-ethoxynitrophenylcarbamide are obtained. These crystals are soluble in chloroform and, on evaporation after the addition of a drop of acetic acid, characteristic crystals are obtained. If dilute nitric acid is used in place of the concentrated acid the "dulcin" does not dissolve, but the mass gradually becomes permeated with crystals of the nitro-compound and under the microscope there is the appearance of a marked effervescence. "Dulcin" is soluble in concentrated sulphuric acid or glacial acetic acid and is deposited as a micro-crystalline precipitate from such solutions on the addition of water or alkali. W. G.

**The Vitali Reaction for Cocaine.** PAUL HARDY (*J. Pharm. Chim.*, 1921, [vii], **24**, 325—330).—Pure cocaine, and most sub-

stituted cocaines, yield a yellow coloration with the Vitali test in the cold; *iso*atropylcocaine, however, yields a violet coloration, and the presence of a small quantity of this substance in certain specimens of cocaine causes these to give a violet coloration with the test. When the reaction mixture is heated, pure cocaine produces at most a slight yellow coloration. W. P. S.

**Morphine, Codeine, and Narcotine in Indian Opium.** JITENDRA NATH RAKSHIT (*Analyst*, 1921, **46**, 481—488).—The morphine content of the bulk of Indian opium is between 8·5 and 10·5%. The B.P. process for estimating morphine is inefficient in India owing to the high temperature which prevails. The U.S.P. process is better and compares favourably with the author's polarimetric process (*Analyst*, 1918, **43**, 321). The solubility of codeine and narcotine has been determined in various solvents at temperatures between 20° and 100°. Methods have also been worked out for the estimation of codeine and narcotine, for which the original should be consulted. H. K.

**Estimation of Tannin and Colouring Matters in Wines.** W. FRESENIUS and L. GRÜNHÜT (*Z. anal. Chem.*, 1921, **60**, 406—417).—One hundred c.c. of the wine is evaporated to expel alcohol, cooled, diluted to 100 c.c. and 50 c.c. of this solution are treated with a few grams of pure animal charcoal; after some hours, the mixture (a further quantity of charcoal must be added if all the colour has not been removed) is diluted to 1 litre, filtered, and 400 c.c. are diluted to 1 litre, treated with 10 c.c. of sulphuric acid, (*d* 1·11), and 30 c.c. of indigo solution (3 grams of indigo dissolved in 20 c.c. of sulphuric acid and diluted to 1 litre) and the mixture is titrated with permanganate solution. Twenty c.c. of the de-alcoholised wine not treated with charcoal are titrated in a similar manner. The difference between the two titrations is a measure of the tannin and colouring substances in the wine. The permanganate solution should contain 1·33 grams of potassium permanganate per litre and be standardised against 10 c.c. of *N*/10-oxalic acid solution; the volume of permanganate solution used is divided into 0·0416 to obtain the tannin value of 1 c.c. of permanganate solution. W. P. S.

**Determination of the Size of Particles. Attempts to Explain the Formation of Layers in Clay Turbidities and their Use in Soil Analysis.** ERNST UNGERER (*Kolloid Chem. Beihefte*, 1921, **14**, 63—95).—The layers in clay suspensions are brought about solely by the size and weight of the suspended particles, so that each layer corresponds with particles of a definite size. The turbidity between two layers contains particles uniformly dispersed. Layers are formed both in solutions containing electrolytes and in solutions which do not contain electrolytes, but a high concentration of a coagulating electrolyte will probably prevent the formation of layers. The individual layers either rise or fall with a uniform velocity, and from the rate of falling or rising the size of the particles in a given layer may be calculated by means of Stokes's law. J. F. S.

## General and Physical Chemistry.

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**Refraction of Light at Corresponding Temperatures.** W. Herz (*Z. physikal. Chem.*, 1921, **98**, 175—180).—A theoretical paper in which from the examination of the data for a large number of substances it is shown that the refractive index of all substances has the same value 1·126 at the critical temperature. The formulæ of Gladstone and Dale, and of Lorentz and Lorenz yield approximately the same specific refraction values for this temperature. It is also shown that at other comparable temperatures the refractive indices approximate to the same value, although in these cases considerable differences do occur. Thus at the boiling point, ten liquid substances give a mean value of 1·335 for the refractive index, the extreme values being 1·348 and 1·320. J. F. S.

**The Spectrochemistry of Aliphatic Dienes with Conjugated Double Bonds.** K. von Auwers and H. Westermann (*Ber.*, 1921, **54**, [*B*], 2993—2999).—The physical constants of a number of carbinols and the corresponding dienes are recorded. The specific exaltations in the cases of the latter substances with "undisturbed, doubly disturbed, and singly disturbed" conjugation are $E\Sigma_{Refr.}$ +2·0, +1·4, and +0·9 and $E\Sigma_{Disp.}$ +50%, +43%, and +35%, respectively. The boiling points of the dienes are depressed by branching of the chain, but raised by the approximation of the methyl group to the double bond; this regularity is not always very definitely marked. The density of isomeric compounds increases relatively greatly when the methyl group is attached to a doubly-bound carbon atom. Similarly, the index of refraction increases with similar alteration in structure; these changes are consonant with those observed with cyclic compounds.

The following constants are recorded: $\Delta^{\beta}$-pentene-$\delta$-ol, b. p. 64°/62 mm., $d_4^{17·95}$ 0·8382, $n_\alpha^{17·95}$ 1·42558, $n_D^{17·95}$ 1·42821, $n_\beta^{17·95}$ 1·43502, $n_\gamma^{17·95}$ 1·44065. $\Delta^{\beta}$-Hexen-$\delta$-ol, b. p. 59°/27 mm., $d_4^{23·3}$ 0·8370, $n_\alpha^{23·3}$ 1·43025, $n_D^{23·3}$ 1·43286, $n_\beta^{23·3}$ 1·43962, $n_\gamma^{23·3}$ 1·44510. $\Delta^{\beta}$-Heptene-$\delta$-ol, b. p. 63°/11 mm., $d_4^{14·4}$ 0·8422, $n_\alpha^{14·4}$ 1·43698, $n_D^{14·4}$ 1·43965, $n_\beta^{14·4}$ 1·44620, $n_\gamma^{14·4}$ 1·45176. $\epsilon$-Methyl-$\Delta^{\beta}$-hexen-$\delta$-ol, b. p. 75°/45 mm., $d_4^{19}$ 0·8411, $n_\alpha^{19}$ 1·43539, $n_D^{19}$ 1·43788, $n_\beta^{19}$ 1·44478, $n_\gamma^{19}$ 1·45045. $\zeta$-Methyl-$\Delta^{\beta}$-hepten-$\delta$-ol, b. p. 67°/11 mm., $d_4^{15·2}$ 0·8354, $n_\alpha^{15·2}$ 1·43679, $n_D^{15·2}$ 1·43926, $n_\beta^{15·2}$ 1·44585, $n_\gamma^{15·2}$ 1·45127. $\eta$-Methyl-$\Delta^{\beta}$-octen-$\delta$-ol, b. p. 85°/12 mm., $d_4^{14·5}$ 0·8402, $n_\alpha^{14·5}$ 1·44202, $n_D^{14·5}$ 1·44448, $n_\beta^{14·5}$ 1·45114, $n_\gamma^{14·5}$ 1·45651. $\delta$-Methyl-$\Delta^{\gamma}$-heptene-$\epsilon$-ol, b. p. 66°/17 mm., $d_4^{17·9}$ 0·8525, $n_\alpha^{17·9}$ 1·44525, $n_D^{17·9}$ 1·44792, $n_\beta^{17·9}$ 1·45454, $n_\gamma^{17·9}$ 1·46018. $\delta$-Methyl-$\Delta^{\gamma}$-octen-$\epsilon$-ol, b. p. 89°/16 mm., $d_4^{19·5}$ 0·8495, $n_\alpha^{19·5}$ 1·44576, $n_D^{19·5}$ 1·44838, $n_\beta^{19·5}$ 1·45490, $n_\gamma^{19·5}$ 1·46059.

$\Delta^{\beta\delta}$-Pentadiene, b. p. 43°, $d_4^{13·6}$ 0·6887, $d_{20}^{13·6}$ 0·685, $n_\alpha^{13·6}$ 1·42991, $n_D^{13·6}$ 1·43443, $n_\beta^{13·6}$ 1·44655, $n_\gamma^{13·6}$ 1·45694, $n_D^{20}$ 1·4309. $\Delta^{\beta\delta}$-Hexadiene, b. p.

80°, $d_4^{15\cdot05}$ 0·7237, $d_{20}^{15\cdot05}$ 0·720, $n_\alpha^{15\cdot05}$ 1·44962, $n_D^{15\cdot05}$ 1·45420, $n_\beta^{15\cdot05}$ 1·46651, $n_\gamma^{15\cdot05}$ 1·47764, $n_D^{20}$ 1·4514. $\Delta^{\beta\delta}$-Heptadiene, b. p. 107°, $d_4^{16\cdot3}$ 0·7341, $d_{20}^{16\cdot3}$ 0·731, $n_\alpha^{16\cdot3}$ 1·45101, $n_D^{16\cdot3}$ 1·45543, $n_\beta^{16\cdot3}$ 1·46695, $n_\gamma^{16\cdot3}$ 1·47735, $n_D^{20}$ 1·4534. $\zeta$-Methyl-$\Delta^{\beta\delta}$-heptadiene, b. p. 117°, $d_4^{15\cdot5}$ 0·7361, $d_{20}^{15\cdot5}$ 0·733, $n_\alpha^{11\cdot5}$ 1·44887, $n_D^{15\cdot5}$ 1·45302, $n_\beta^{15\cdot5}$ 1·46397, $n_\gamma^{15\cdot5}$ 1·47379, $n_D^{20}$ 1·4505. $\eta$-Methyl-$\Delta^{\beta\delta}$-octadiene, b. p. 149°, $d_4^{11\cdot6}$ 0·7515, $d_{20}^{11\cdot6}$ 0·751, $n_\alpha^{11\cdot6}$ 145427, $n_D^{11\cdot5}$ 1·45831, $n_\beta^{11\cdot6}$ 1·46903, $n_\gamma^{11\cdot6}$ 1·47812, $n_D^{20}$ 1·4553. $\epsilon$-Methyl-$\Delta^{\beta\delta}$-hexadiene, b. p. 104°, $d_{20}^{19\cdot7}$ 0·745, $n_D^{20}$ 1·4606, (i) $d_4^{19\cdot7}$ 0·7439, $n_\alpha^{19\cdot7}$ 1·45659, $n_D^{19\cdot7}$ 1·46117, $n_\beta^{19\cdot7}$ 1·47340, $n_\gamma^{19\cdot7}$ 1·48433, (ii) $d_4^{19\cdot65}$ 0·7473, $n_\alpha^{19\cdot65}$ 1·45589, $n_D^{19\cdot65}$ 1·46037, $n_\beta^{19\cdot65}$ 1·47262, $n_\gamma^{19\cdot65}$ 1·48316. $\beta$-Methyl-$\Delta^{\alpha\gamma}$-butadiene, b. p. 34°, $d_4^{18\cdot8}$ 0·6826, $d_{20}^{18\cdot8}$ 0·682, $n_\alpha^{18\cdot8}$ 1·41902, $n_D^{18\cdot8}$ 1·42309, $n_\beta^{18\cdot8}$ 1·43422, $n_\gamma^{18\cdot8}$ 1·44405, $n_D^{20}$ 1·4224. $\delta$-Methyl-$\Delta^{\gamma\epsilon}$-heptadiene, b. p. 131°, $d_4^{24\cdot4}$ 0·7598, $d_{20}^{24\cdot4}$ 0·763, $n_\alpha^{24\cdot4}$ 1·45610, $n_D^{24\cdot4}$ 1·46003, $n_\beta^{24\cdot4}$ 1·47125, $n_\gamma^{24\cdot4}$ 1·48103, $n_D^{20}$ 1·4625. $\delta$-Methyl-$\Delta^{\gamma\epsilon}$-octadiene, b. p. 150°, $d_4^{20\cdot3}$ 0·7708, $d_{20}^{20\cdot3}$ 0·771, $n_\alpha^{20\cdot3}$ 1·46206, $n_D^{20\cdot3}$ 1·46617, $d_\beta^{20\cdot3}$ 1·47724, $n_\gamma^{20\cdot3}$ 1·48708, $n_D^{20}$ 1·4663. $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene, b. p. 70°, $d_4^{22\cdot1}$ 0·7239, $d_{20}^{22\cdot1}$ 0·725, $n_\alpha^{22\cdot1}$ 1·43307, $n_D^{22\cdot1}$ 1·43703, $n_\beta^{22\cdot1}$ 1·44758, $n_\gamma^{22\cdot1}$ 1·45704, $n_D^{20}$ 1·4382. H. W.

[**Substitution Processes**]. K. von Auwers (*Ber.*, 1921, **54**, [*B*], 3000—3003).—A reply to K. H. Meyer (A., 1921, i, 853). The view that the methyl group causes optical exaltation cannot be maintained. In certain of the examples quoted by Meyer the differences lie within the limits of experimental error, whereas in other examples readily polymerised substances, for instance, acrylic acid and its esters, have been chosen and the data obtained are not due to the unimolecular forms. H. W.

**The Molecular Refraction of Aromatic Hydrocarbons and "Aromatic" Carbon.** K. von Auwers (*Ber.*, 1921, **54**, [*B*], 3188—3194).—In a recent communication (A., 1921, ii, 473), von Steiger has endeavoured to show that the molecular refraction of hydrocarbons can be calculated more accurately from linking refractions than from atomic refractions and he has postulated that all C—C bonds and all C—H bonds in aromatic hydrocarbons are equivalent among themselves but different from the corresponding values in the aliphatic series. This mode of calculation appears to the author to be unsound theoretically, since the atomic refraction of aromatic hydrogen as deduced from the molecular refraction of benzene, diphenyl, and naphthalene, in these circumstances is negative, whilst also the "linking refraction" for $(C—H)_{ar}$ falls with decreasing wave-lengths. Von Steiger has illustrated his arguments by citing the cases of benzene, diphenyl, and naphthalene, and the agreement between the observed and calculated values is excellent. Unfortunately, the data quoted for naphthalene are incorrect, and the amended figures show that the presumption of additivity is not fulfilled. Further, the data for the three hydrocarbons are not directly comparable, since they are obtained under widely-differing conditions; when due allowance is made for this factor, it is found to be impossible to deduce constant atomic or linking refractions. The molecular refractions

of homologues of benzene, and other aromatic hydrocarbons cannot be calculated from von Steiger's aromatic and aliphatic linking refractions, since the differences between the observed and calculated values increase more and more with increase in the number of side-chains.

The fundamental idea in von Steiger's refractometric hypothesis and thermochemical theories (A., 1920, ii, 355) is the existence of a practically tervalent "aromatic" carbon atom of the graphite type which differs from the quadrivalent "diamond" carbon atom of the paraffins (cf. Debye and Scherrer, A., 1917, ii, 437). To the author, this view of the varying valency appears to be misleading. The supposed ter- and quadri-valency of the carbon atom does not, as in the case of other elements, correspond with different stages of oxidation or different electric charges; the atom is invariably quadrivalent and the apparent variation is caused by alteration in the distribution or compensation of its affinity. H. W.

**The Mechanism of Continuous Luminous Radiation.** J. DUCLAUX (*Compt. rend.*, 1921, **173**, 1355—1357).—The author has previously put forward the hypothesis (cf. *ibid.*, 1914, **158**, 1879) that the emission and absorption of the continuous spectrum depend on the establishment or rupture of chemical valencies. Evidence in support of this hypothesis is now given. W. G.

**The Spectrum of Fluorine.** WILLIAM R. SMYTHE (*Astrophys. J.*, 1921, **54**, 133—139).—With a discharge passing between gold electrodes, the ultra-violet region of the fluorine spectrum was photographed through a fluorite window, the gas having been prepared by the electrolysis of potassium hydrogen fluoride and purified by being passed through sodium fluoride and a freezing trap. Ten fluorine lines, all in the red, were observed and tabulated with an accuracy of $\pm 0{\cdot}1$ Å. An impurity which was supposed to have the composition $CF_4$ was observed following a flare back from the charcoal chamber. The approximate positions of nine heads of bands between $\lambda$ 4829 and $\lambda$ 6525 were observed in this spectrum.

CHEMICAL ABSTRACTS.

**Arc-cathode Spectra.** ARTHUR ST. C. DUNSTAN and BENJAMIN A. WOOTEN (*Astrophys. J.*, 1921, **54**, 65—75).—The spectra of strontium, barium, lithium, copper, and lead were observed when the vapours of the metals were introduced into a direct current arc by means of an alternating current arc placed below it in the same enclosure. It was shown that by cooling the electrodes alternately, the intensity of the metallic lines remained, as before, greater at the cathode than at the anode when the metal was introduced into the arc symmetrically; neither was the effect due to electrolytic or electrostatic separation. Since the phenomenon is fully developed in 1/120 second, the transference of vapour from one electrode to the other must be of little importance. The light appears to be due chiefly to bombardment of the metallic vapour by electrons from the cathode. Whilst the lines of all

metals are stronger at the cathode, the difference decreases with increasing atomic weight. CHEMICAL ABSTRACTS.

**The Electric Furnace Spectrum of Scandium.** ARTHUR S. KING (*Astrophys. J.*, 1921, **54**, 28—44).—The spectrum of a pure sample of scandium oxide was observed in the carbon arc and in the electric furnace through the range λ 3015—6559 Å. The furnace was operated at the usual low gas pressure, and temperatures of 2200°, 2250°, and 2600° were used. A table gives the classification of 257 lines with respect to their behaviour in the arc and at various furnace temperatures. Some 25 lines are indicated as being enhanced in the arc; 150 are enhanced in the furnace. The 29 arc-flame lines belong to the latter class, some of them showing moderate strength at all temperatures, whilst others increase in intensity more or less rapidly with increasing temperature. These lines are not due to oxidation, but the bands, on the other hand, are quite probably due to the oxide. Lines which appear at a low temperature and those enhanced in the furnace are weak or lacking in the general solar spectrum but prominent in that of sun-spots. The Zeeman effect for scandium lines is large and apparently uniform in sunspot spectra, although laboratory observations have not as yet been made. Scandium oxide fused in the furnace seemed to form a carbide with the graphite of the boat. The glossy black residue became a greyish-brown powder on exposure to the air, presumably reabsorbing oxygen. CHEMICAL ABSTRACTS.

**Wave-length Measurements in Arc Spectra Photographed in the Yellow, Red, and Infra-red.** F. M. WALTERS, jun. (*Bureau of Standards, Sci. Papers*, 1921, **17**, No. 411, 161—177).—Observations were made with a grating spectrograph of 640 cm. radius and 299 lines per mm. The photographic plates were sensitised to yellow, red, or infra-red light with pinacyanol and dicyanin. The wave-lengths of silver, aluminium, gold, bismuth, cadmium, mercury, lead, antimony, tin, and zinc are given in international units and to 0·01 Å. The longest wave-length measured is that at 10395 Å. in the spectrum of cadmium. The work is compared with previous results of others and discrepancies are accounted for as arising from impurities, ghosts, or overlapping spectra of higher orders. CHEMICAL ABSTRACTS.

**Extension of the Ultra-violet Spectrum and the Progression with Atomic Number of the Spectra of Light Elements.** R. A. MILLIKAN (*Proc. Nat. Acad. Sci.*, 1921, **7**, 289—294).—The results of an investigation of the extreme ultra-violet radiations emitted by the second ring or shell of electrons in the atoms of atomic number 2 to 13 (helium to aluminium) are recorded. The ultra-violet spectrum has been photographed down to λ=136·6 Å. in the case of aluminium and to λ=149·5 Å. in the case of copper. The $L_a$ lines of aluminium, magnesium, and sodium are found at 144·3 Å., 232·2 Å., and 372·2 Å., respectively. Aluminium emits no radiations when excited by condensed sparks in a vacuum between

144·3 Å. and 1200 Å., where the $M$ spectrum due to the three outer electrons begins. The chief lines below 2000 Å. due to the three outer electrons of aluminium are 1379·7, 1384·5, 1605·9, 1612·0, 1671·0, 1854·7, and 1862·7 Å. Magnesium is like aluminium, there is a blank between its $L_a$ line at 232·2 Å. and the lines due to the two outer electrons which begin at 1700 Å. The lines measured below 2000 Å. are 1735·2, 1737·9, 1751·0, and 1753·7 Å. Sodium emits no lines between the $L$ line 376·5 Å. and the lines due to the single $M$ electron which have their convergence wave-length at 2412·63 Å. The spectrum due to the six $L$ ring electrons of oxygen begins at 230 Å. and extends with much complexity and strength up to 834·0 Å., where the strongest line is found; above this point the lines are few in number and relatively faint. The ratio of the $K/L$ frequency for oxygen is about 35. The strongest oxygen lines are 321·2, 374·3, 507·8, 525·7, 554·2, 599·5, 610·1, 616·7, 625·2, 629·6, 644·0, 703·1, 718·5, and 834·0 Å. The spectrum of the four $L$-ring electrons of carbon begins at 360·5 Å. and extends with much complexity and strength up to 1335·0 Å., where the strongest line lies; above this point the lines are widely scattered and relatively weak. The ratio of the $K/L$ frequency in carbon is about 30. The spectrum due to the five $L$-ring electrons of nitrogen is simple; it begins at 685·6 Å. and reaches a maximum at 1085·3 Å. The only other strong lines of nitrogen are 685·6 Å., 916·2 Å., and 991·1 Å. The ratio of the $K/L$ frequency is 34·8. In the case of fluorine, a strong line appears at 657·2 Å. and a second at 607·2 Å.; these are the only lines thus far identified as coming from the seven $L$-ring electrons of fluorine. The spectrum from the three $L$-ring electrons of boron is very simple. It consists of 676·8, 760·0, 1624·4, two doublets, 2164·2, 2166·2, and 2496·9, 2497·8, and a single spark line, 3451·5 Å. The ratio of the frequency $K/L$ is 37. The spectrum of the two $L$-ring electrons of glucinum begins at 2175 Å. and finishes in its $L_a$ doublet at 3130·6 and 3131·2 Å. Similar experiments with lithium reveal no lines between the shortest wave-lengths measurable by the present method and the familiar series due to its single $L$-ring electron the $L_a$ line of which is at 6708 Å., and its convergence wave-length at 2299 Å. The progression shown in these optical spectra is simple and very like that exhibited by $X$-ray spectra.

J. F. S.

**The Structure of the Elements of Mean Atomic Number.** A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 1458—1461).—An extension of previous work (cf. A., 1921, ii, 669), further results being given for gold and new measurements of the $L$ series for cerium and antimony.

W. G.

**The Structure of the Bismuth Lines.** H. NAGAOKA and Y. SUGIURA (*Astrophys. J.*, 1921, **53**, 339—348).—The light resulting from the bo[...] ectronic current was observed by [...] ke plate crossed with one of quart[...] rating. For the line 4722 the f[...] were confirmed and

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seven weak negative satellites were discovered, showing the line to have the general structure common to lines of heavy metals. The principal component is probably multiple, its constituents varying in relative intensity. The line λ 4122 has four strong components. The line λ 4308 consists of two principal lines separated by 0·350 Å., each being a narrow doublet; there are also two faint satellites. The authors point out some constant frequency differences and suggest that these may be interpreted in terms of the quantum theory. CHEMICAL ABSTRACTS.

**The Zeeman Effect.** H. R. WOLTJER (*Chem. Weekblad*, 1921, **18**, 677—682).—A paper written in connexion with the twenty-fifth anniversary (October 31st, 1921) of the first announcement of Zeeman's discovery. The importance and subsequent developments of his work are discussed at some length. S. I. L.

**Anisotropy of Molecules.** C. V. RAMAN (*Nature*, 1922, **109**, 75—76).—An extension to direct visual observations is described of the method whereby it has been shown photographically (Lord Rayleigh, A., 1920, ii, 574) that the light scattered by molecules is, in general, not completely polarised when observed in a direction transverse to the pencil of light traversing the gas. With carbon dioxide, the effect is conspicuous, and visual determinations of its magnitude have been made. Similar evidence that the molecules of gases are not spherically symmetrical and are anisotropic in their properties is furnished by observations on the polarisation of light of the sky; liquids also show an imperfect polarisation attributable to anisotropy. A. A. E.

**Sols with Non-spherical Particles.** H. ZOCHER (*Z. physikal. Chem.*, 1921, **98**, 293—337).—The double refraction discovered by Diesselhorst, Freundlich, and Leonhardt (A., 1916, ii, 65) with flowing vanadium pentoxide sols has been found in the following sols: Soap solntion, clay suspensions, sols of silver cyanate, benzopurpurin, "benzo-brown," primulin, sodium alizarinsulphonate, alizarin, *p*-azoxyphenetole, *p*-azoxyanisole, anthracene, cerasin-orange, and aniline-blue. Some observations on the spacial partition of the double refraction in agitated sols showed that in the eddies phenomena were observed which exhibited many analogies to the behaviour of uniaxial crystals in convergent light. These observations serve as methods for determining the flowing-double refraction and pleochroism and for determining the character of the sols. The rotation of the dark cross in eddies in opposition to the polarisation direction shows the direction of flow does not always need to correspond with the main vibration direction of the light. The coincidence of the dark cross with the direction of polarisation in old vanadium pentoxide sols and soap solutions is attributed to the bending of the doubly refracting particles. The sign of the double refraction of soap solutions varies with the age and concentration of the sol. The change in the sign of the double refraction is explained as follows: Colloidal particles in the form of short rods must arrange themselves with their symmetry axis

n the direction of flow, particles in the form of leaflets must arrange themselves with the axis of symmetry at right angles to this direction. If now, in the process of ageing, the rods pass into leaflets, then the optical character of the direction of flow must at first be the same as that of the colloidal particles and afterwards of the opposite sign. Aniline-blue sols, prepared by pouring an alcoholic solution of the dye into water, show on flowing a strong negative double refraction in the red, negative pleochroism in the region orange to green, and a positive double refraction in the blue. Anomalous interference bands are produced by this anomalous behaviour. The optical anisotropy produced by a magnetic field has the opposite sign, that is, the colloidal particles arrange themselves at right angles to the lines of force. On the other hand, they arrange themselves parallel to the electrical lines of force. The negative double refraction of benzopurpurin can be made to disappear by heating. The addition of electrolytes causes the double refraction to reappear on cooling. The coagulum obtained by the addition of an excess of electrolyte gives a doubly refracting sol on peptisation if the addition of the electrolyte was slow or if the original sol was doubly refracting, but if the coagulation took place rapidly or if the original sol was isotropic, there will be no double refraction. When acidified, double refracting red sols may be changed into double refracting blue sols. The strong pleochroism has always a negative sign, and the particles of the sols are diamagnetic. The double refraction of vanadium pentoxide sols disappears more slowly the older and more concentrated the sol. Very concentrated old vanadium pentoxide sols and concentrated, electrolyte-poor benzopurpurin solutions show a persistent double refraction similar to that of the crystalline liquids. The view of Diesselhorst and Freundlich (*loc. cit.*), that the growth of non-spherical particles is not a crystallisation but an aggregation of non-spherical primary particles in parallel layers, is confirmed, with the addition that the primary particles may be crystalline and that eventually they may undergo crystalline processes. J. F. S.

**Recent Advances in Stereochemistry.** B. K. Singh (*J. Proc. Asiatic Soc. Bengal*, 1921, **17**, 213—230).—A general account of the historical development of stereochemistry and a discussion of the relation between optical activity and chemical constitution. Particular consideration is given to optical activity in homologous series, the effect of conjugated unsaturation, and of position isomerism on optical activity. The Walden inversion is also discussed. H. W.

**Investigations on the Fundamental Law of Photochemistry.** P. Lasarev (*Z. physikal. Chem.*, 1921, **98**, 94—97).—A theoretical discussion of work previously published on the bleaching of dyes by light (A., 1912, ii, 219; *Ann. Physik*, 1907, [iv], **24**, 661). The experiments on the bleaching in the presence of oxygen under increased pressures (up to 150 atm.) are particularly considered. The fundamental law for the bleaching of dyes has the form

$-dC/dt = \alpha_0(1-e^{-KC})(1-e^{-K_1C_1})$, in which $C$ is the concentration of the dye, $K$ a constant proportional to the absorption constant $C_1$ and $K_1$ similar values for the substance non-sensitive to light and $\alpha$ the photochemical constant. It is assumed that in the reaction, during the absorption of light, an electron from the first Bohr orbit springs over to the furthest orbit. It is shown that the total absorption of light is proportional to the absorption of the largest (ionised) atoms. The increase in volume during photochemical reactions is explained by the assumption that the light inasmuch as it occasions an increase in the volume of the atoms by effecting the electron spring, brings about an increase in the gaseous volume. J. F. S.

**New Measurements of Precision in the X-Ray Spectrum** M. SIEGBAHN (*Compt. rend.*, 1921, **173**, 1350—1352).—By the use of three spectrographs, each adapted to a particular spectral region it was possible to measure a wave-length with an accuracy of 0·01—0·005%, and by this means the wave-length of the copper line $K\alpha_1$ was found to be $1537{\cdot}36\times10^{-11}$ cm. in a vacuum. A more precise instrument is described the readings of which are accurate to within 0·002%, and with this the value of $\lambda$ for $K\alpha_1$ was found to be $1537{\cdot}302\times10^{-11}$ cm. W. G.

**Spectrographic Study of the De-intensifying of Barium Platinocyanide in the Villard Effect.** A. ZIMMERN and E. SALLES (*Compt. rend.*, 1922, **174**, 80).—Fluorescent screens which have undergone the Villard effect can be regenerated by exposure to diffused light. It is shown that the radiations capable of destroying the Villard effect are found in four principal bands of almost equal breadth. The first is entirely in the infra-red, the second in the greenish-yellow, the third in the blue, and the fourth in the ultra-violet. W. G.

**The Theory of Absorption of X-Rays by Matter and the Principle of Correspondence.** LOUIS DE BROGLIE (*Compt. rend.*, 1921, **173**, 1456—1458).—An expression for the atomic coefficient of absorption of a substance for a radiation of wave-length $\lambda$ has previously been given (cf. A., 1920, ii, 208) in which the constant, $\alpha$, was defined by the hypothesis that, for the possible changes of internal configuration of an atom placed in a system in thermodynamic equilibrium at the temperature $T$, the probability $A_{12}$ of the return of the atom from a configuration of energy $\epsilon_1$ to a configuration of less energy, $\epsilon_2$, is proportional to $\epsilon_1-\epsilon_2$ and also to the absolute temperature in such a way that $A_{12}=\alpha(\epsilon_1-\epsilon_2)T$. A mathematical proof of the truth of this hypothesis and a means of calculating the constant $\alpha$ are given, and it is shown that the coefficient of the Bragg-Pierce law is a universal constant capable of being expressed as a function of the constants of the electron and of the radiation. W. G.

**Calculation of the X-Ray Absorption Frequencies of the Chemical Elements. I and II.** WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1921, **7**, 260—267; 267—273).—In the first paper,

the author has calculated the $K$ critical absorption frequencies of the elements magnesium, sulphur, calcium, iron, selenium, molybdenum, tin, cerium, dysprosium, tungsten, lead, and uranium on the basis of the Rutherford-Bohr theory of the structure of atoms and the mechanism of radiation. The assumption is made that the electrons are distributed in circular orbits, which do not lie in planes passing through the nucleus of the atom. In order to estimate the forces exerted on an electron in one orbit, $A$, due to the electrons in the parallel orbit, $B$, it is assumed that they are the same as if the charges are concentrated, half at the nearest point to the orbit $A$ and half at the point furthest from $A$. A series of values is obtained which are in fair agreement with those observed. In the second paper, it is assumed that the forces are the same as if the electricity of the electrons in the orbit $B$ is uniformly distributed along the orbit. The values calculated on the second assumption are somewhat smaller than those of the first calculations. J. F. S.

**The Laws of Absorption of X-rays.** F. K. Richtmyer (*Physical Rev.*, 1921, **18**, 13—30).—An experimental study of the absorption of $X$-rays by water (oxygen), aluminium, copper, molybdenum, silver, and lead, each over a great part of the range of wave-lengths 0·093 Å. to 0·95 Å. The longest of these waves is shorter than the critical $K$ absorption wave-length of oxygen, aluminium, or copper, and falls between $K$ and $L$ for molybdenum, silver, and lead. Rays from a Coolidge tube were analysed by a spectrometer with a sodium chloride crystal, and the intensity was measured by ionisation of methyl bromide. Scattered and fluorescent radiation from the absorbing screen were suppressed by placing the screen in front of the spectrometer slit nearest the tube. Detailed tables and curves of the results are given. The mass-absorption coefficients, $\mu/\rho$, of these substances is given by $\mu/\rho = F\lambda^3 + (\sigma/\rho)$ where $\lambda$ is wave-length and $\sigma/\rho$ is the mass-scattering coefficient, except in the region close to $\lambda_K$ on the short-wave-length side, where the equation gives values which are somewhat too large, the error being greater as the difference between $\lambda$ and $\lambda_K$ is smaller. For each substance $F$ has a constant value for $\lambda < \lambda_K$ and another much smaller constant value for $\lambda > \lambda_K$. The mass-scattering coefficient is independent of wave-length, and is, to a first approximation, the same for all elements. The atomic-absorption coefficient is given by $\mu_a = 2{\cdot}29 \times 10^{-27} N^4\lambda^3 + \sigma_a$, where $N$ is the atomic number and $\sigma_a$ the atomic-scattering coefficient, for $\lambda < \lambda_K$. No trace of the suggested "$J$" absorption discontinuity was found. At 0·093 Å., $\mu/\rho$ for water is still much greater than for the hard rays of radium-$C$. Chemical Abstracts.

**The Luminescence of certain Oxides Sublimed in the Electric Arc.** E. L. Nichols and D. T. Wilber (*Physical Rev.*, 1921, **17**, 707—717).—Thin films of metallic oxides were obtained by subliming the metal or one of its salts from the crater of a direct-current carbon arc on to a metal disk. Oxides prepared by sublimation are found to respond to excitation by cathode rays.

The shift in colour with increasing temperature in luminescence is in general to the violet. The effect of pressure on luminescence is discussed. The most active oxides were those of calcium, magnesium, zinc, zirconium, silicon, and aluminium.

CHEMICAL ABSTRACTS.

**Anode Rays of Glucinum.** G. P. THOMSON (*Nature*, 1921, **107**, 395).—The method of positive ray analysis applied to lithium (Aston, A., 1920, ii, 344) has been extended to glucinum and found to yield a well-marked parabola corresponding with a single charge and an atomic weight $9{\cdot}0 \pm 0{\cdot}1$(Na=23). No second parabola was observed which could be ascribed with certainty to glucinum, but it is doubtful if a line of intensity one-tenth that of the first could have been detected. No indication was found which would suggest that the atom of glucinum can lose two electrons under the prevailing experimental conditions. A. A. E.

**Reactions in Penetrating Radium Radiation and in Ultra-violet Radiation Filtered by Quartz Glass. II. The Hydrogen Peroxide Equilibrium set up in Radium Radiation.** ANTON KAILAN (*Z. physikal. Chem.*, 1921, **98**, 474—497; cf. A., 1912, ii, 10, 522; 1920, ii, 576).—Radiation from 0·1 gram of radium metal after passing through 1 mm. of glass into 100 c.c. of water in contact with air produces a solution containing $6\times10^{-6}$ gram-equivalent of hydrogen peroxide; in the presence of $0{\cdot}01N$-sulphuric acid the amount of hydrogen peroxide becomes $10^{-4}$, and in $1{\cdot}0N$-acid the amount is $5\times10^{-4}$ gram-equivalent. In the last-named solution $6\times10^{12}$ and in the first $3\times10^{12}$ molecules of hydrogen peroxide are formed per second. These values are considerably less than those obtained nine or ten years ago, and reasons for the discrepancy are advanced. A comparison of the values obtained for the velocity of formation of hydrogen peroxide then and now with the rate of formation by other reactions which have been obtained in a similar manner to the present shows that both in aqueous and in non-aqueous solutions, when the decomposition of hydrogen peroxide is neglected, the number of molecules of hydrogen peroxide formed is of the same order as that of the ion pairs absorbed from the radiation by the medium. In ultra-violet light from a quartz glass lamp under similar conditions, the reduction of the peroxide concentration by increase in the hydrogen-ion concentration is less than in the radium rays, whilst the decomposition of hydrogen peroxide is more than one hundred times greater than in the radium rays. J. F. S.

**Stationary Electron Vibrations without Radiation Resistance.** A. D. FOKKER (*Physica*, 1921, **1**, 107—109).—It is theoretically shown that a Bohr atom with electrons revolving in closed paths may be free from radiation resistance without violating the principles of the classical theory. CHEMICAL ABSTRACTS.

**The Radioactivity of the Oxides of Uranium.** CHARLES STAEHLING (*Compt. rend.*, 1921, **173**, 1468—1471; cf. A., 1920, ii, 5).—In continuation of previous work (*loc. cit.*), it is shown that

the radioactivity of the green oxide, which has been restored to its original value, commences to diminish as before. The restoration of activity may be brought about by simple calcination without passage through ammonium uranate. During this process of restoration, the oxide undergoes loss in weight, due, for the most part, to the removal of moisture. The black oxide which shows little loss in activity also shows little loss in weight or alteration in activity on calcination. The author considers that the green oxide exposed to the air in thin layers undergoes hydration as well as loss in activity, the hydration diminishing the superficial density of the uranium atoms. The black oxides obtained by calcination at high temperatures do not hydrate and show little or no decrease in radioactivity. These facts tend to confirm the existence of a definite black oxide, which is probably an allotropic modification of the green oxide. W. G.

**Isotopy of the Radio-elements and Meitner's Nucleus Model.** MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 161—167).—A theoretical paper in which, on the basis of Meitner's nuclear hypothesis (A., 1921, ii, 293), the author has subdivided isotopes into four groups. These are termed isotopes of the first, second, third, and fourtb order. Isotopes of the first order have the same nuclear charge and arrangement of the outside electrons, but different nuclear mass, total number of nuclear constituents, arrangement of the nuclear constituents, number of each kind of nuclear constituent, and probability of disintegration; radium and meso-thorium-I illustrate this group. Isotopes of the second order have the same nuclear charge, arrangement of the outside electrons, nuclear mass, and total number of nuclear constituents, but different numbers of each kind of nuclear constituent, arrangement of the nuclear constituents, and probability of disintegration. An example of this class is furnished by ionium and uranium-*Y*. Isotopes of the third order differ only in the arrangement of the nuclear constituents and the probability of disintegration, all other properties being identical; this is the case with radium-*D* and actinium-*B*. Isotopes of the fourth order are identical in all the properties mentioned; no examples of this class are known. J. F. S.

**Calculation of the Branching Relationships for Dual α-Disintegration and the Meitner Nucleus Model.** MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 168—171; cf. Meitner, A., 1921, ii, 293).—A theoretical paper in which it is shown that the method of calculation adopted by Smekal (A., 1921, ii, 149) for determining the branching relationship is so closely dependent on the assumptions made as to the structure of the radioactive nucleus, that it cannot possibly be of general use. The branching relationship cannot be calculated by this method, since it leads to inaccurate values which lead to results opposed to the experimental data. The agreement found for the branching relationship by this method for the uranium, radium, thorium,

and actinium families with the experimentally determined value for this relationship is accidental. J. F. S.

**Emissivity of Iron and Copper.** K. LUBOWSKY (*Elektro techn. Z.*, 1921, **42**, 79—81).—The emissivity of both bright an blackened iron and copper was determined. Curves are give showing the effect of convection currents obtained from a fla plate of the material, first perpendicular to, and second in th direction of the air stream. Expressed in watts per sq. cm. per 1 of temperature excess, the emissivity varies from $0{\cdot}75\times10^{-3}$ t $1{\cdot}5\times10^{-3}$ under the various conditions. CHEMICAL ABSTRACTS.

**The Effects of Impurities on the Ionisation Potential Measured in Thermionic Valves.** L. S. PALMER (*Radio Rev* 1921, **2**, 113—125).—The method of investigation used is based o a study of the current-voltage curves measured in hard and so 3-electrode tubes. The details of the method have been given in previous paper. Certain bends in these curves are interpreted a being due to the bombardment of the filament by positive ion The ionisation potentials of helium, mercury, and argon have thu been determined. There are variations in the values for th ionisation potentials obtained in helium. These are ascribed t impurities, and the amount of impurity active accords with th values found by Horton in helium (A., 1919, ii, 210; 1920, ii, 660 1921, ii, 672). This effect of the impurity also explains the lov values of the potentials obtained by Stead and Gossling (A., 1920 ii, 659). The characteristic of the soft 3-electrode tube can be use to determine the resonance and ionising potentials of the containe gas. The nature of the gas and presence of the impurities can b determined from the critical points of the characteristics. Method of measuring ionisation potentials are liable to error if impuritie are present. Horton's previous work is confirmed and the resul has been extended to argon with traces of mercury. The valu of the ionisation potential decreases slightly with increase of ga pressure, causing changes in the characteristics similar to those fo impurities. A number of critical potentials obtained for heliun and argon are given. CHEMICAL ABSTRACTS.

**Estimation of the Radium Content of Radioactive Luminous Compounds.** E. A. OWEN and WINIFRED E. PAGE (*Proc Physical Soc.*, 1921, **34**, 27—32).—The absorption of $\gamma$-radiatio in zinc sulphide has been measured by different methods, and it value found to be approximately the same by all. No indica tion was observed of the occurrence of an abnormal absorptio when the radioactive salt was mixed with the sulphide. A tabl has been drawn up which gives the values of the ratio of the tru to the apparent radium content for tubes of different diameter filled with a radioactive luminous compound. This table applie to a compound the apparent density of which is 2·03 grams per c.c The value of the absorption of $\gamma$-radiation from radium has bee measured for zinc sulphide (0·101), barium sulphate (0·079), barium chloride (0·100), barium carbonate (0·046), lead monoxide (0·294),

bismuth sesquioxide (0·206), and uranium pentoxide (0·315). The absorption coefficients are given in brackets in $cm.^{-1}$. The mass absorption coefficient has been calculated in each case, and it is shown that the barium salts have nearly the same value, the mean value being 0·053. J. F. S.

**Electrical Conductivity of Salts and Mixtures of Salts.** A. Benrath and K. Drekopf (*Z. physikal. Chem.*, 1921, **99**, 57—70).—The specific conductivity of molten mixtures of potassium sulphate with sodium sulphate, magnesium sulphate, potassium fluoride, and lithium sulphate respectively has been determined over the whole range of compositions and from the results relationships to the diagram of condition are drawn. It is shown that the conductivity isotherm can be deduced only to a small extent from the diagram of condition. It is also shown that the point at which the eutectic appears is a well defined conductivity point. Pure salts as well as salt compounds change their conductivity with temperature according to the formula $\log k=a+bT$. This formula is not generally applicable to mixtures of salts and mixed crystals; attempts to obtain a theoretical basis for the formula gave the relationship: $\log k''+bT''=$const. The formula of Tubandt, $\log K=c-d/T$, is not generally applicable. For the complete explanation of the phenomena, other factors, particularly the viscosity, must be known and taken account of in the calculation. J. F. S.

**The Electrical Conductivity of Anhydrides of the Higher Fatty Acids.** D. Holde and Ida Tacke (*Chem. Ztg.*, 1921, **45**, 1246—1247; cf. A., 1921, i, 842).—The values previously given for the molecular conductivity of oleic anhydride and oleic acid in acetone, on being adjusted to a dilution of 50 and 8 respectively gave $2{\cdot}015\times10^{-4}$ and $0{\cdot}53\times10^{-4}$. If it is assumed that these two compounds are only slightly dissociated, that is, that the molecular conductivity increases proportionally to the square root of the dilution, the calculated figure for $\lambda_{50}$ for oleic acid becomes $1{\cdot}33\times10^{-4}$, a figure not differing very greatly from that of the anhydride; the difference may be due to impurities in the acetone used. A. R. P.

**Measurement of Dielectric Constants.** J. F. King and W. A. Patrick (*J. Amer. Chem. Soc.*, 1921, **43**, 1835—1843).—A bridge method for the measurement of dielectric constants is described in which an arrangement consisting of an electron tube, a condenser, and an induction coil connected in a circuit serve as the source of alternating current of symmetrical wave form. Preliminary measurements of the dielectric constant of mixtures of ethyl alcohol with benzene, ethyl ether, and carbon tetrachloride respectively up to 100% by weight of alcohol, are recorded. The dielectric constant increases with each addition of alcohol to the other constituent in a fairly regular manner. J. F. S.

**Electrical Moments of Carbon Monoxide and Dioxide Molecules.** Hans Weigt (*Physikal. Z.*, 1921, **22**, 643).—The

dielectric constants of carbon monoxide and carbon dioxide and their dependence on temperature have been determined with the object of ascertaining by means of the Debye theory the electrical moment of the two gases. The values obtained are $\mu_{CO_2}=(0{\cdot}1420\pm0{\cdot}0017)\times10^{-18}$, $\mu_{CO}=(0{\cdot}1180\pm0{\cdot}0016)\times10^{-18}$, both of which are in good agreement with that calculated from the Lorentz-Lorenz formula. J. F. S.

**Application of the Theory of Allotropy to Electromotive Equilibria. IV.** A. SMITS (*Z. physikal. Chem.*, 1921, **98**, 455—459; cf. A., 1915, ii, 217; 1916, ii, 77; 1917, ii, 232).—The author offers a corrected interpretation of that published ("Theorie der Allotropie," Leipzig, 1921, 403—405) for the electromotive behaviour of metals as soon as they are attacked by acids. The *E.M.F.* of *M*/2-zinc sulphate dissolved in water, 0·05*N*-sulphuric acid, 0·1*N*-, 0·5*N*- and 1·0*N*-sulphuric acid, and *N*-potassium sulphate has been determined at 18° in an atmosphere of nitrogen. The results show that the potential of zinc is not effected by the presence of acid below 0·5*N*, and from this point upwards the potential is only changed by 2 millivolts. Similar experiments are described with zinc chloride in hydrochloric acid solutions; here it is shown that a concentration of hydrochloric acid of 0·1*N* is without influence on the potential, but that 0·5*N* and 1·0*N* cause a change in the *E.M.F.* of 0·021 and 0·038 volt, respectively. J. F. S.

**Electromotive Behaviour of Aluminium.** A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1921, **27**, 579—582).—A reply to Smits, in which the author maintains his previous assertions (cf. this vol., ii, 20). J. F. S.

**Electromotive Behaviour of Metallic Compounds with Electron Conductivity.** G. TRUMPLER (*Z. physikal. Chem.*, 1921, **99**, 9—56).—Metallic or mixed conducting binary compounds combined with the metallic component as conductor and immersed in a solution of a salt of the metal which is saturated with the compound, have a zero potential when measured against the metallic component in the same solution. The formula put forward previously by Haber for such cases has been confirmed in the case of cuprous iodide, and cuprous, lead, and silver sulphides. It is also shown that metallic and mixed conducting compounds combined with the metallic component as conductor possess the same potential as an indifferent electrode (platinum) when immersed in a solution saturated with these substances and containing the negative component both as ion and in the free condition. A necessary condition in this case is the stability of the compound towards the metallic conductor and the solution. This has been investigated in the case of lead, cupric, cuprous, silver, and ferrous sulphide against sodium sulphide and polysulphide solutions. If in the last case pure electrolytes are used, the free negative component has no influence on the potential against the solution; this is much more dependent on the concentration of the components in the solution. This has been shown in the cells $Ag|AgBr|KBr,Br_2$(sat.); $Ag|AgI|KI,I_2$(sat.). In the case of the

mixed conducting silver sulphide in the presence of free sulphur the potential lies between that of the pure components. This potential is a characteristic of the mixed conductor. The three forms of conductors, metallic, mixed, and electrolytic, are characterised by the potential relationship obtained by the above-named measurements. From the different behaviour of the metallic and electrolytic conductors (compounds) with respect to the influence of the negative component on the potential relations as obtained by the above method, a fundamental difference of the internal structure is deduced, according to which in the pure metallic conducting compounds the space lattice points are occupied by atoms or molecules and not by ions. They appear, in opposition to electrolytes, to be non-polar. It is shown that pure cuprous sulphide is an electrolyte, or a mixed conductor in which the metallic component of the conductivity is very small. The passivity of lead sulphide in solutions of lead salt has been investigated and a process for activating the substance is put forward. The data in the literature on the solubility of lead sulphide and cupric sulphide are corrected. The electrometric determination of the solubility of lead sulphide is not possible on account of the complete passivity of the lead electrode in sulphide solutions. The solubility product of lead sulphide has been determined approximately from the solubility in hydrochloric acid and the value $[Pb^{\cdot\cdot}]\cdot[S'']=5\times10^{-29}$ obtained. It is shown that cupric sulphide is not stable in sodium sulphide and that in the presence of copper only cuprous sulphide can exist in sodium sulphide solution, and consequently the measurement of the copper potential in sodium sulphide solution does not give the solubility product of cupric sulphide (cf. Knox, A., 1908, ii, 830). The solubility product of cuprous sulphide is found to be $[Cu^{\cdot}]^2\cdot[S'']=2\times10^{-47}$. J. F. S.

**The "Salt Error" of the Quinhydrone Electrode.** S. P. L. Sørensen, M. Sørensen, and K. Linderstrøm-Lang (*Compt. rend. Trav. Lab. Carlsberg,* 1921, **14**, No. 14, pp. 31).—Biilmann's quinhydrone electrode (A., 1921, ii, 372) gives, in the presence of sodium chloride, too small a potential (with $3\cdot99N$-sodium chloride + $0\cdot01N$-hydrochloric acid 0·6931 volt instead of 0·7044 volt at 18°). This is due to a lowering of the solubility of quinhydrone and can be overcome by saturating the salt solution with quinhydrone and with one of its constituents, for example, with quinol. This and various other questions are discussed theoretically in detail, and the theory is verified by experiments. G. B.

**The Quinhydrone Electrode.** Einar Biilmann and Hakon Lund (*Ann. Chim.*, 1921, [ix], **16**, 321—340).—It has previously been shown (A., 1921, ii, 372) that aqueous solutions of quinhydrone may be used for the preparation of reversible electrodes with very constant potential, which may serve to determine hydrogen-ion concentrations in solutions which are one-tenth molar. Concordant results are not obtained with stronger solutions. It is possible to construct electrodes, however, in which the electromotive

reaction is a transformation of one solid body into another soli body. The preparation of such electrodes with benzoquinone quinhydrone and with quinol–quinhydrone is described. Suc electrodes have hydrogenation potentials $\pi_{18}$=0·7562 and 0·617 respectively. They may be used for measurements over a wid range of hydrogen-ion concentration. W. G.

**Electromotive Force produced by the Relative Displace ment of an Electrode and an Electrolyte.** Stéfan Procopi (*J. Chim. Physique*, 1921, **19**, 121—134).— It is found that the mov ment of an electrode in a liquid gives rise to an *E.M.F.* of mov ment which is general for all metallic electrodes. The dimensio of this *E.M.F.* are determined only by the solution pressure the metal and the osmotic pressure of the metallic ion in t solution. The effects produced when a series of metals is move in water, nitric acid, sulphuric acid, salts of the metals, an potassium hydroxide have been measured. The phenomenon explained by the existence of a layer of solution round the electro of composition different from that of the rest of the solution. Th leads to a relationship between the photoelectric *E.M.F.* and that movement, and makes it possible to find the effect of moveme on the electrical resistance of liquids. J. F. S.

**The Overvoltage of the Mercury Cathode.** Edgar Newber (T., 1922, **121**, 7—17).

**Theory of the Electrolytic Ionic Condition and the Calc lation of the Electrolytic Solution Constants, and of th Related Quantities from the Chemical Relationships.** Ka Fredenhagen (*Z. physikal. Chem.*, 1921, **98**, 38—69).— theoretical paper in which it is shown that neither Arrhenius electrolytic dissociation theory nor Nernst's theory of solutio tension furnishes any information on the nature of the ionic co dition or the nature of ionic dissociation. Neither of these theori can be directly deduced from the facts of inorganic chemistr and they do not bring these facts into relationship with one anothe The author has put forward an hypothesis of the ionic conditio and the electrolytic solution constants which removes the abov named defects and shows how ordinary thermal dissociatio passes into electrolytic dissociation. The hypothesis also show how the solution constants of the elements, and the partition an dissociation constants of chemical compounds may be calculate from the chemical relationships of the compounds and element and from a factor which expresses the condition of the solven The hypothesis permits a qualitative deduction of the electric and dielectrical behaviour of conductors of the second class.

J. F. S.

**An Electrolytic Current Intensification Effect, a New trolytic Displacement Effect, and the Connexion betwee olysis and the Emission of Electrons in a Vacuum. II** Hinstein and F. Klement (*Z. physikal. Chem.*, 1921, **99** cf. A., 1921, ii, 729).—A continuation of work previous

published (*loc. cit.*). It is shown that in a closed circuit by means of superimposed alternating current a stronger direct current can be produced, the work from which can be greater than that of the alternating current used to generate it. The action of a high frequency current on an electrolytic cell is not a specific high frequency action; qualitatively, it is the same as that of a low frequency current. All passivity phenomena, both anodic and cathodic, show on superposing an alternating current on the direct current a decrease of the direct current polarisation, and thereby allow themselves to be used as detectors or current intensifiers. Using the commutator method, an intensification of two hundred times has been obtained and the experiments indicate that this may be still further increased. A new experiment with a highly evacuated electron tube is described, which indicates that after removal of the polarisation it is possible to generate cathode rays with low potentials and cold electrodes. J. F. S.

**Applicability of the Gas Laws to Strong Electrolytes. II.** J. N. BRØNSTED (*K. Danske Videnskab. Selskab., Math.-fys. Medd.*, 1920, **3**, 1—21; cf. A., 1920, ii, 78).—By a modification of the original electrometric method, consisting in the use of a streaming electrode, *E.M.F.* determinations have been carried out with one electrolyte dissolved in a concentrated solution of another. Cells of the type: $\mathrm{Ag,AgCl}\left|\begin{array}{l}\text{solvent } (n-c_1)\\ \text{chloride } (c_1)\end{array}\right|\begin{array}{l}\text{solvent } (n-c_2)\\ \text{chloride } (c_2)\end{array}\left|\mathrm{AgCl,Ag}\right.$ and $\mathrm{Ag}\left|\begin{array}{l}\text{solvent } (n-c_1)\\ \text{silver salt } (c_1)\end{array}\right|\begin{array}{l}\text{solvent } (n-c_2)\\ \text{silver salt } (c_2)\end{array}\left|\mathrm{Ag}\right.$ were employed. Support is afforded to the theory that the simple gas laws are valid for ions present in salt solutions the concentrations of which are large in comparison with that of the ions concerned. Conditions under which the law fails to apply are discussed, and the results of Loomis, Essex, and Meacham (A., 1917, ii, 353), that slight changes in the activity coefficient occur with varying concentrations, are confirmed. CHEMICAL ABSTRACTS.

**Newer Investigations on the Anomaly of the Strong Electrolytes.** LUDWIG EBERT (*Jahrb. Radioaktiv. Elektronik*, 1921, **18**, 134—196).—An alphahetical bibliography of the work on strong electrolytes is given. The whole subject of the behaviour of strong electrolytes is discussed under the headings (i) chief anomalies, and (ii) the hypothesis of complete dissociation of the strong electrolytes and the activity of electrical forces between the ions. J. F. S.

**Transport Numbers of Sulphuric Acid by the Concentration Cell Method.** ALFRED L. FERGUSON and WESLEY G. FRANCE (*J. Amer. Chem. Soc.*, 1921, **43**, 2150—2160).—A method is described for the determination of the transport numbers of a uni-bivalent electrolyte by measurement of the potentials of concentration cells. The transport number of the anion of sulphuric acid for concentrations between $0{\cdot}1M$ and $0{\cdot}01M$ has been measured and found to be $0{\cdot}1868\pm0{\cdot}0007$ at 25°. This value is compared

with the values obtained by other investigators. It is shown that the dissociation values determined from freezing-point data are more satisfactory for calculating the potentials of concentration cells than those obtained from conductivity data. A correction to the formula for the potential of a concentration cell has been developed which takes into account the undissociated part of the acid. It is shown that the concentration cell method is entirely satisfactory for the determination of the transport numbers of sulphuric acid. J. F. S.

**Influence of Gelatin on the Transport Numbers of Sulphuric Acid.** ALFRED L. FERGUSON and WESLEY G. FRANCE (*J. Amer. Chem. Soc.*, 1921, **43**, 2161—2171).—The effect of gelatin on the transport numbers of gelatin has been investigated. It is shown that the addition of sulphuric acid up to 20% increases the transport number of the anion of sulphuric acid (0·1—0·01*M*) from 0·187 in the absence of gelatin to 0·685 in the presence of 20% gelatin. The effective concentration of 0·1*M* and 0·01*M* sulphuric acid solution is reduced by the addition of gelatin. The conductivities of sulphuric acid are reduced by the addition of gelatin. An hypothesis is put forward to account for the action of gelatin in the presence of electrolytes. J. F. S.

**Electro-osmosis.** A. H. W. ATEN (*Chem. Weekblad*, 1921, **18**, 690—692).—The theory of electro-osmosis of liquids through porous solids is discussed, and the volume passing in unit time shown to be directly proportional to the current density, the dielectric constant of the liquid and the potential difference between the liquid and the porous material, and inversely proportional to the viscosity and conductivity of the liquid. The various attempted technical applications of the phenomenon, and of kataphoresis (which term is restricted to the motion of solid particles suspended in a liquid under the influence of the electric field) are described. S. I. L.

**Some Electro-osmotic Experiments with de Haen's Membrane Filters.** P. H. PRAUSNITZ (*Kolloid Z.*, 1921, **29**, 293—309).—The electro-osmosis of water, solutions of ammonia, sulphuric acid, ammonium sulphate, sodium sulphate, potassium ferricyanide, and aluminium sulphate, through de Haen filters for varying size of pores, has been investigated at 25° and under a pressure of 43 cm. of water. It is shown that the de Haen filters are particularly well adapted to the study of the influence of electrolytes on electro-endosmosis. Filters of medium-sized pores (Nos. 20 and 320) when 5 cm. thick allow 100—500 c.c. of water to pass per hour under the pressure used in the experiments. Distilled water ($\lambda = 6 \times 10^{-6}$) travels toward the cathode through the membrane under a current of 100 volts and about 0·1 ampere at the rate of 1—2 litres per hour. The addition of sulphuric acid to the anode compartment, or any addition of thorium chloride or aluminium sulphate, reduces the electro-endosmosis to values below that of water and in cases may produce even a weak anodic endosmosis. In

other cases, the addition of electrolytes brings about an increased cathodic endosmosis, in which the amount of water transported varies with the time the current is flowing and the nature and concentration of the electrolyte. It is shown that, in general, with an electrical conductivity of $200—400\times10^{-6}$ and a consumption of energy of 0·01—0·06 *KWH*/litre of transported liquid, 8—16 litres/hour of liquid can be made to pass through a diaphragm of 100 cm.$^2$. It is not always necessary that the electrolyte should pass through the membrane as such; particularly in the case of ammonia it is shown that the addition of the base to the cathode compartment can bring about a very considerable endosmosis of the water, which is to be attributed to the wandering in the opposite direction of those ions which are responsible for the discharging of the membrane. The transport of the $SO_4$-ion throngh a de Haen membrane from negative to positive compartments brings about a considerable passage of water from the positive to the negative compartment. In every case there is an optimum electrolyte concentration, and if this is exceeded anomalies occur which are found to be connected closely with the electrical conductivity. The discharge of the membrane is held to be due in all probability to the adsorption of hydroxyl ions, for all processes which effect a reduction of the hydroxyl-ion concentration also effect a reduction of the electro-endosmosis (cf. *D.R.-P.* 333575, 1919). J. F. S.

**Attainment of Constant High Temperatures.** E. Moser (*Z. angew. Chem.*, 1921, **34**, 625).—The apparatus or object to be maintained at constant temperature is immersed in paraffin contained in a cylindrical glass vessel surrounded by an outer glass vessel of similar shape but enlarged to a spherical form at the bottom to accommodate a liquid of suitable boiling point, which is kept in ebullition so that its vapour surrounds the inner vessel. The two vessels are sealed together round the top except where a tube serves to connect the vaponr jacket with a reflux condenser. The lower end of the condenser tube projects downwards for some distance into the vapour jacket and the vapour enters it through a lateral orifice. The end of the tube is drawn out to a jet and disposed vertically above the boiling liquid. By this arrangement the condensed liquid is warmed again before it falls back into the jacket and is prevented from falling on the hot walls of the vessels. Liquids of high boiling point, such as ethyl benzoate, b. p. 212·5°, have been successfully used in the outer vessel. J. H. L.

**The Expansions of some Refractory Materials at High Temperatures.** B. Bogitch (*Compt. rend.*, 1921, **173**, 1358—1360).—The expansion curves for bauxite, clay, silica, chromite, and magnesia over the temperature range 0° to 1600° are given. The smallest expansion was shown by the bauxite, which is suitable for use in furnaces subject to sudden changes in temperature. Silica showed the most irregular expansion; it expanded rapidly up to 600° and then only very slowly, and above 1000° showed a slight contraction. The curve shows two singular points at 210°

and 570° respectively, which are the transformation points of cristobalite and quartz. Furnaces constructed with such bricks must only be heated up very slowly, the temperature rise being less than 50° per hour. The curve for the clay bricks is intermediate between the curves for bauxite and silica. Magnesia and chromite showed the biggest expansions, and such bricks are only suitable for the construction of furnaces in continuous work. W. G.

**Coefficient of Expansion of Molten Salts.** W. Herz (*Z. physikal. Chem.*, 1921, **98**, 98—102).—In previous papers (A., 1914, ii, 25, 245; 1921, ii, 381) it has been shown that Mendeléev's equation is true for the expansion of normal organic liquids. In the present paper, the equation has been applied to the molten inorganic substances, sodium molybdate, lithium nitrate, sodium nitrate, rubidium bromide, cæsium nitrate, potassium tungstate, cæsium iodide, potassium molybdate, sodium tungstate, rubidium fluoride, cæsium sulphate, and thallous nitrate. The data employed are taken from the work of Jaeger (A., 1918, ii, 33). The densities calculated by the Mendeléev formula agree in most cases to about 1 per 1800 with the experimental values. The only cases where divergence is shown are thallous nitrate and sodium tungstate, and here it is not much greater than in the other cases. The density values calculated by the Mendeléev equation are compared with those calculated by Jaeger (*loc. cit.*) by a single constant formula for cæsium iodide and rubidium fluoride, and by a two constant formula for cæsium sulphate and the value of the single constant Mendeléev formula demonstrated. J. F. S.

**General Methods for the Determination of the True Molecular Constitution of Pure Substances and their Mixtures.** Mario Basto Wagner (*Z. physikal. Chem.*, 1921, **98**, 81—93).—A theoretical paper in which the author differentiates between the thermodynamics of mixtures treated in connexion with their independent components and the thermodynamics of mixtures treated in connexion with their true components. The advantages and drawbacks of both methods of treatment are explained and the nature of the results obtainable is pointed out in each case. The various properties which may be used in the determination of constitution are enumerated and their application is indicated. These include volume, heat change, vapour pressure, solubility, freezing point, boiling point, specific heat, compressibility, thermal coefficient of expansion, and osmotic pressure. The properties, dielectric constant, viscosity, refraction, and surface tension do not permit conclusions being drawn which may be used in the second method of treatment. J. F. S.

**Thermodynamics of Mixtures. IX.** Mario Basto Wagner (*Z. physikal. Chem.*, 1921, **98**, 151—156; cf. A., 1921, ii, 375).—A theoretical paper in which the theory of the heat of mixtures is developed on the basis of the thermodynamics of mixtures treated in connexion with the true components (cf. preceding abstract).

J. F. S.

**Theory of Equations of State. II.** MARIO BASTO WAGNER (*Z. physikal. Chem.*, 1921, **98**, 244—251; cf. preceding abstract).—The hypothesis developed previously is extended. The present paper deals with the theory of the heat of vaporisation and the internal pressure. J. F. S.

**Equation of Condition of Nitrogen at Small Pressures and Low Temperatures.** R. BARTELS and A. EUCKEN (*Z. physikal. Chem.*, 1921, **98**, 70—79).—The equation of condition of nitrogen has been measured by means of a constant pressure gas thermometer between the temperatures 90° and 76° Abs. and between the pressures 0·5 and 1·0 atm. The results are represented by means of an empirical formula for the correction quantity $B'$ of the form $v=RT/p-RTB'$. This formula has been used to calculate the molecular heat of nitrogen for the ideal gas conditions, and the value 6·873 obtained for $C_p$. This value is 0·07 cal., or 1% lower than that (6·944 cal.) demanded by the classical theory, whilst the Berthelot equation of condition leads to a value 0·2 cal. lower than the classical value for the temperature 92° Abs. A comparison of the reduced $B'$ values for a range of temperature shows that the curves for hydrogen and nitrogen cannot be brought into coincidence, but that at low temperatures they diverge. J. F. S.

**Equation of Condition. II. Principal Equation of Condition. III. Principal Equation of Condition and the Equation of Condition for Individual Substances. IV. Compressibility Equations of Liquids.** A. WOHL (*Z. physikal. Chem.*, 1921, **99**, 207—225, 226—233, 234—241; cf. A., 1914, ii, 430).—A series of theoretical papers in the first of which the author further develops the equation of condition previously published (*loc. cit.*). The various relationships brought out by this equation are considered and compared with the equations of van der Waals and Kamerlingh Onnes. In the second paper, equations of condition are developed and considered for helium, hydrogen, water, and ethyl alcohol. The third paper deals with compressibility equations for liquids, particularly highly compressed substances. The substances ethyl ether, carbon dioxide, and hydrogen are considered. J. F. S.

**Extension of Ebullioscopy and its Application to Binary Mixtures.** ERNST BECKMANN and OTTO LIESCHE (*Z. physikal. Chem.*, 1921, **98**, 438—454).—The authors have combined the Raoult equation $P=P_0[N/(N+n)]$ with Dalton's law $P=B[N'/(N'+n')]$ to form the equation $P_0[N/(N+n)]=B[N'/(N'+n')]$ and shown that this equation may be used generally in the ebullioscopy of binary mixtures, and may be extended to meet complicated cases, since the determination of the absolute boiling point fixes the value of $P_0$ with the help of vapour pressure tables or formulæ. The introduction of the boiling point difference $\Delta$ and the ebullioscopic constant $E$ leads to a special ebullioscopic equation

$\Delta = E(n - n')$, which may only be used for small $\Delta$ values. If in either of the above equations $n$ or $n'$ is given the value zero, the two limiting cases are obtained, in which the second component (represented by small letters) is non-volatile or is not soluble in the first component. J. F. S.

**A Vapour Pressure Formula with a General Integration Constant.** F. A. HENGLEIN (*Z. physikal. Chem.*, 1921, **98**, 1—13).—A theoretical paper in which the constants of a previously published rule (A., 1920, ii, 732) for the comparison of the vapour pressure curves of two substances, $\log T_1 = a \log T_2 + b$, have been brought into relationship with the Trouton constants. From this relationship a vapour pressure formula has been deduced which contains two specific constants and has the form $\log p_{(atm.)} = -k/T^n + 4{\cdot}6222$. The formula holds, in comparison with other two constant vapour pressure formulæ, over greater temperature ranges and is characterised by the fact that the integration constant is the same for all substances. The index $n$ is shown to be equal to $\lambda/(v-v')p \, . \, K$ where $K$ has the same value for all substances, and consequently $\lambda/(v-v')p$ may be calculated from the above formula; on the other hand, $n$ may be determined from $\lambda/(v-v')p$ or $\lambda/RT$. To calculate the actual formula, two vapour pressure determinations are necessary, or the knowledge of one vapour pressure point and the molecular latent heat of vaporisation at the same pressure. The formula is shown to be equally true for sublimation pressures, and it may also be applied to decomposition pressures. J. F. S.

**Theory of Binary Mixtures. VII. Mixtures of Ethyl Ether and Bromoform.** F. DOLEZALEK and M. SCHULZE (*Z. physikal. Chem.*, 1921, **98**, 395—429; cf. A., 1920, ii, 32).—The vapour pressure of a series of mixtures of ethyl ether and bromoform has been determined at 25° and 75°; the contraction on mixing, the coefficient of expansion, and the density of the mixtures have been determined at 25°. The results show that on mixing the components a mutual partial complex formation occurs. The resulting compound consists of one molecule of ether and one molecule of bromoform; it occurs in the solution in a dissociated condition and on heating it decomposes. Bromoform itself is strongly associated, but with decreasing concentration the association decreases. The vapour pressure was determined by a new static method. A theory is developed whereby the molecular constitution may be calculated from the vapour pressure measurements. From two measured vapour pressures the combination constant $K$ and the association constant $k$ were determined, and from these the molecular constitution of the mixture was calculated for 25°. The results show that at 25° bromoform consists of 65% of bimolecules and that in the mixture of 1 mol. of ether and 1 mol. of bromoform, 23% of the equi-molecular compound is present. The vapour pressure for all mixtures has been calculated from the molecular composition, and found to be in good agreement with the experimental values. A marked contraction occurs on mixing

ether and bromoform: the contraction curve is strongly depressed on account of the association of the bromoform. The contraction has been calculated on the basis of the theory and found to agree with the observed contraction. From the coefficient of expansion the contraction at 15°, 20°, and 30° has been calculated. From the contraction at 25°, the density of the mixtures was calculated, and the results show that the measurement of volume change by the differential method is the most exact for the measurement of easily volatile liquid mixtures. J. F. S.

**Vapour Pressure of Binary Mixtures.** GERHARDT C. SCHMIDT (*Z. physikal. Chem.*, 1921, **99**, 71—86).—A new simple static method of measuring the vapour pressure of liquids is described. It is shown that the dynamic method of measuring the vapour pressure of mixtures gives only moderate results and then only when the experiments are made under definite conditions, and it is inferior in every way to the new static method. The vapour pressures of the following mixtures, benzene–ethyl ether, benzene–chloroform, benzene–methyl acetate, methyl acetate–ethyl acetate, benzene–carbon disulphide, benzene–toluene, toluene–carbon disulphide, ethyl alcohol–methyl alcohol, benzene–methyl alcohol, chloroform–carbon disulphide, and acetone–chloroform have been measured up to a pressure of 4 atmospheres. By plotting the molecular compositions as abscissæ and the vapour pressures as ordinates, it is found that at all temperatures (20—100°) mixtures of ethyl alcohol and methyl alcohol give a straight line. Mixtures of benzene and ether and of benzene and chloroform give approximately straight lines up to 30°, but at higher temperature curves which are convex to the abscissa axis, and the higher the temperature the greater the convexity. Mixtures of acetone and chloroform at 0° give a straight line, and at higher temperatures curves convex to the abscissa axis, which become more convex as the temperature is raised. Mixtures of benzene and toluene, ethyl acetate and methyl acetate, and benzene and methyl acetate at low temperatures give straight lines, but at higher temperatures the curves are concave to the abscissa axis and the concavity becomes greater as the temperature is raised. Mixtures of benzene and carbon disulphide, toluene and carbon disulphide, chloroform and carbon disulphide, and benzene and methyl alcohol, give at 0° curves which are concave to the abscissa axis, and the higher the temperature the greater the concavity, this being particularly noticeable in the case of benzene–methyl alcohol. From the fact that the higher the temperature the greater the concavity or convexity, the conclusion can be drawn that for every liquid mixture there is a temperature at which the relationship between the vapour pressure and the molecular composition may be represented by a straight line, generally speaking this occurs at low temperatures. It is shown that a series of deductions from Dolezalek's theory of binary solutions, which refer to the influence of temperature on the course of the isotherms, are not confirmed by the experiments. Consequently the theory cannot be maintained. J. F. S.

**Intersecting Vapour Pressure Curves and Deductions therefrom.** CARL VON RECHENBERG (*Z. physikal. Chem.*, 1921, **99**, 87—104).—A large number of pairs of substances are recorded for which the vapour pressure curves intersect. From a comparison of the intersecting vapour pressure curves the following conclusions are drawn. All liquid and solid substances consist of large molecular complexes of undetermined variable composition of different stability, and present as many classes of compounds as they have different molecular types. Every individual compound behaves in a characteristic manner. The division of liquids into associated and non-associated groups from surface tension measurements is incorrect. All compounds are associated, but the so-called associated compounds are more loosely combined. The sub-division only separates the most divergent compounds, but does not take account of the intermediate and transition compounds. A table is drawn up of the various aggregates according to the increase of vapour pressure with increase of temperature. The table is very similar to Rothmund's solubility table, from which it follows that vapour formation and solubility are parallel phenomena and must be due to the same oause. J. F. S.

**Vaporisation of Solutions of Liquid Pairs possessing Intersecting Vapour Pressure Curves.** CARL VON RECHENBERG (*Z. physikal. Chem.*, 1921, **99**, 105—115; cf. preceding abstract).—The Bancroft rule, that liquids with intersecting vapour pressure curves form solutions with a characteristic point, has been confirmed, when notiee is taken of the fact that the property of the characteristic solution only obtains inside a limited pressure region. A large number of homogeneous mixtures with intersecting vapour pressure curves are tabulated with the minimum boiling point and the concentration of the characteristic fraction at 760 mm.

J. F. S.

**Distillation and Rectification.** L. GAY (*Chim. et Ind.*, 1921, **6**, 567—578; cf. this vol., ii, 85).—In order to obtain the maximum efficiency from a column, ceteris paribus, the higher the temperature of the initial mixture the lower should be the level of its introduction into the distillation apparatus. This level should be such that an initial liquid or gaseous mixture meets a liquid or gaseous mixture of approximately the same composition in the column. If the liquid mixture is at its boiling point, or rather if the gaseous mixture is at its condensation point, then the composition of the two mixtures is identical. The determination of the minimum intensity of heat and the minimum number of compartments of the column necessary for an initial gaseous mixture has been carried out in a similar manner to that used for an initial liquid mixture (*loc. cit.*), and applied to the separation of practically pure water and alcohol from any gaseous mixture of water and alcohol at 95°. The determination of the minimum intensity of heat necessary to remove a trace of impurity from a liquid has also been carried out. F. M. R.

**Heat of Formation of Silver Iodide.** HUGH STOTT TAYLOR and WILLIAM THEODORE ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 2014—2017).—Braune and Koref's calorimetric measurement of the heat of formation of silver iodide (A., 1914, ii, 536), using *N*-potassium cyanide instead of 3*N*-solutions as solvent for silver iodide, have been repeated. The result 15,100 cal. per mol. of silver iodide has been obtained, which confirms Braune and Koref's value. J. F. S.

**Relationship between Heat of Solution and Heat of Fusion of Organic Substances.** GEORG GEHLHOFF (*Z. physikal. Chem.*, 1921, **98**, 252—259).—The heat of solution of naphthalene, diphenyl, diphenylamine, azobenzene, α-naphthylamine, β-naphthylamine, urethane, paraffin (wax), nitronaphthalene, nitrophenol, *m*-dinitrobenzene, phenol, menthol, thymol, pyrogallol, resorcinol, citric acid, and chloral hydrate has been determined in 1—3% solutions in the solvents water, benzene, ethyl ether, alcohol, carbon disulphide, acetone, amyl acetate, aniline, chloroform, and acetic acid. The results show that for a series of substances, particularly hydrocarbons, aromatic amines, urethane, and azobenzene, the heat of solution in various solvents is practically identical with the heat of fusion. Organic substances containing the hydroxyl group give very different values for the heat of solution and the heat of fusion, whilst substances containing the nitro-group take up an intermediate position between the other substances. The heat of solution of the sodium, potassium, and ammonium haloids has been determined in aqueous solution, and the results are discussed in connexion with the structures and space lattices of these salts.

J. F. S.

**Heats of Solution and of Transformation of the Acido- and Aquo-cobalt Pentammines.** ARTHUR B. LAMB and JOHN P. SIMMONS (*J. Amer. Chem. Soc.*, 1921, **43**, 2188—2199).—A method of calorimetry has been developed in which only observations on a silver coulometer and of time and electrical resistance are required. It is shown that the same cobalt sulphide, $Co_2S_3$, is produced by the action of sodium sulphide on chloro- and aquo-pentamminecobalt chloride in aqueous solution. The solubility of chloropentamminecobalt chloride in water at 0°, 30°, and 50° has been determined, and the values 2·244, 6·047, and 10·01, respectively, have been obtained in grams per litre. The heat of solution has been calculated from these data and the value 13,440 cal. obtained, which is in fair agreement with the experimental value, 12,400 cal. The heats of solution of a number of acido- and aquo-pentamminecobalt salts in water have been measured. The following values are found at 25°, in cals., chloro-chloride, −12,420; aquo-chloride, −6,460; bromo-bromide, −12,660; aquo-bromide, −9,220; nitrato-nitrate, −14,900; and aquo-nitrate, −15,300. The heat of reaction of solutions of pentammine salts with solutions of sodium sulphide has been measured at 25° and that of the solid salts with sodium sulphide solutions calculated. The

following values in cals. at 25° are obtained, chloro-chloride, 15,070; aquo-chloride, 12,930; bromo-bromide, 13,290; aquo-bromide, 11,600; nitrato-nitrate, 12,340, and aquo-nitrate, 11,860. From these results the heat of transformation of the acido-salt to the aquo-salt in each case has been calculated, and the values chloride, 2,140 cal.; bromide, 1,690 cal., and nitrate, 480 cal. have been obtained. J. F. S.

**Heat of Wetting of Silica Gel.** W. A. PATRICK and F. V. GRIM (*J. Amer. Chem. Soc.*, 1921, **43**, 2144—2150).—The heat change occasioned by wetting silica gels with water, ethyl alcohol, benzeue, carbon tetrachloride, and aniline, respectively, has been determined at 25°. The quantity of liquid used in each experiment was 50·07 c.c. and the amount of gel 2·3—2·5 grams. The following values in cals./gram of gel were obtained: water, 19·22; alcohol, 22·63; benzene, 11·13; carbon tetrachloride, 8·42, and aniline, 17·54. The heats of wetting have been discussed and found to be in keeping with the changes of surface energy. J. F. S.

**Viscosity of Gelatin Sols.** ROBERT H. BOGUE (*J. Amer. Chem. Soc.*, 1921, **43**, 1764—1773).—A number of experiments have been effected with gelatin sols to determine the relation between viscosity and concentration. The data obtained have been applied to Hatschek's formula for the viscosity of emulsoids, and it is shown that the value of $A'/A$, representing the volume occupied per unit weight of dispersed phase, is not a constant with varying concentration, but rises regularly to a maximum and thereafter regularly diminishes with increasing concentration. This behaviour is noticed also in the case of other colloids. A tentative explanation is presented based on the effect which increasing concentrations of dispersed phase will have on the surface tension of the dispersion medium. Assuming the equilibrium, surface tension $\rightleftharpoons$ solvation potential, an empirical relation is developed which, with a fair degree of accuracy, defines the equilibrium. At very high concentrations, a reversal of phase probably occurs, at which no expressions yet developed adequately represent the relations involved. A high degree of solvation is shown to be indicated by a high coefficient of viscosity, that is, solvation and viscosity are parallel functions. Isoelectric gelatin at a hydrogen-ion concentration $2\times10^{-5}$ is shown to have the lowest viscosity and the lowest degree of solvation, gelatin chloride at a hydrogen-ion concentration $3{\cdot}1\times10^{-4}$ the highest, and calcium gelatinate at a hydrogen-ion concentration $2{\cdot}5\times10^{-6}$ is intermediate. If an excess of acid is allowed to remain in the gelatin solution, even although the acid be of very low concentration, the viscosity and degree of solvation will be reduced. J. F. S.

**A New Viscostalagmometer for the Estimation of Surface Tension and Viscosity of Liquids of Very Different Limpidity.** I. TRAUBE (*Biochem. Z.*, 1921, **120**, 106—107).—The essential feature consists in the adaptation to the ordinary form of stalagmo-

meter of five interchangeable ground-in mouth-pieces of differing capillary bore, thus allowing measurements to be performed with the same apparatus on liquids of a great range of fluidities.

H. K.

**Ionisation and Surface Activity of Aqueous Solutions of Aliphatic Acids.** WILH. WINDISCH and PHIL. OSSWALD (*Z. physikal. Chem.*, 1921, **99**, 172—188).—The connexion between ionisation and surface activity of organic acids has been investigated. It is shown that of $N/10$-acid or alkali when added to an aqueous solution acts only as a diluent, that is, the surface activity is independent of the hydrogen-ion concentration. Experiments have been made to determine the concentration of acids of different strengths, such as hydrochloric, formic, and acetic acids, which must be added to solutions of nonoic acid so that the same size of drops may be obtained, and also the concentrations of these acids which will produce the same colour with methyl-orange solution. It is shown that free nonoic acid in aqueous solution is 10% dissociated, and therefore the addition of acid increases its surface activity. The simultaneous presence of sodium chloride is without action on the activity. With continued addition of acid, the size of the drops sinks to a constant minimum. A solution of sodium nonoate exhibits a small activity, because through hydrolysis a small quantity of acid exists in the free condition. By the addition of a small quantity of alkali, the free molecules are ionised and the size of the drop sinks to that of water. An addition of hydrochloric acid produces fresh acid molecules, and the size of the drop sinks to a minimum, which is reached when all the aliphatic acid ions have disappeared. Consequently it follows that the surface activity of aqueous solutions of aliphatic acids is due to ionisation processes, and the possibility of calculating the size of the drops due to the action of various additions is pointed out. J. F. S.

**High Pressure due to Adsorption, and the Density and Volume Relations of Charcoal.** WILLIAM D. HARKINS and D. T. EWING (*J. Amer. Chem. Soc.*, 1921, **43**, 1787—1802).—The present paper furnishes evidence in favour of the hypothesis previously expressed (A., 1921, ii, 87) by the authors, which states that the liquids which penetrate into charcoal are compressed by a force due to molecular attraction, which acts as a pressure of many thousand atmospheres (20,000 or more). The present paper shows that it is the liquid in the micro-pores and not the macro-pores which is compressed, and consequently the pressure would probably be much greater than the figure mentioned. Not only charcoal but other porous substances and fine powders should exert this compressive effect, but to a much smaller extent. A number of experiments are described in which the compression is demonstrated by volume changes, but the values measured have not exceeded 72 atms. Ethyl ether, which is much more compressible than water, occupies a volume in charcoal which is

about 10% *less than that occupied by the amount* of water which outside the charcoal is equal in volume to the ether. It is probable that the water in the micro-pores is compressed by about 25% or more, whilst the ether is compressed by 40%. *The liquids in the* macro-pores of the diameter $1·2 \times 10^{-3}$ cm. are not compressed sufficiently to produce a noticeable effect on the volume. The true volume relations in 1 c.c. of a characteristic coconut shell charcoal are 0·28 c.c. micro-pores, 0·18 c.c. macro-pores, 0·54 c.c. carbon, which give a density of 1·60 for the carbon. The density of the lumps of such a charcoal is 0·866. Charcoals which are inactive as adsorbents of gases do not exert a compressive effect on the adsorbed liquids of a sufficiently high magnitude to be very evident, although there appears to be a slight effect of this nature. The densities of the carbon in the two inactive wood *charcoals investigated* are 1·65 and 1·50. When coconut-shell charcoals alone are considered, it is found that the lower the apparent density in an organic liquid, the less is the adsorptive action on vapours, and *it is indicated that this relation may be expected to* hold better the more compressible the liquid which is adsorbed, so that either ethyl ether or pentane or another highly compressible liquid should be used in such tests. Simple thermodynamic equations are given for the heat of immersion or adsorption of a plane surface. Whilst there is probably no definite area of surface inside a lump of charcoal, a definition for an apparent area may be given. The one chosen here is that the apparent area with respect to the heat of immersion is the area of the plane surface of carbon which will develop the same amount of heat on immersion as is equal to that developed by the immersion of 1 gram of the charcoal in the same liquid. Since the film in the charcoal is probably a number of molecules thick, this apparent area is probably larger than corresponds with the carbon surface. This method *indicates that the area of 1 gram of charcoal is 120 sq. metres.* The magnitude of the heat of immersion of liquids on mercury is $3·3 \times 10^{-6}$ cal. for octane and $3·25 \times 10^{-6}$ cal. for *iso*butyl alcohol.

J. F. S.

**The Origin of the Potential Differences Responsible for Anomalous Osmosis.** JACQUES LOEB (*J. Gen. Physiol.*, 1921, **4**, 213—226).—If a collodion bag, coated on the inside with protein (gelatin) separate two identical acid solutions and a neutral salt be added to the inside; the rate of diffusion inwards through the membrane is a minimum at the isoelectric point of the protein, increases with the acidity to a maximum, and then decreases. The potential difference between the two solutions varies similarly. In the absence of protein, these characteristic variations are not obtained. *The anomalous variation of the potential difference is* apparently a consequence of the Donnan equilibrium between solution and protein, and this potential difference causes electrical endosmosis, and hence the irregular rates of diffusion. The potential difference is also influenced by the diffusion potential, but this exists although no protein is present.

W. O. K.

**Penetration of Electrolytes into Gels. III. Influence of the Concentration of the Gel on the Coefficient of Diffusion of Sodium Chloride.** WALTER STILES and GILBERT SMITHSON ADAIR (*Biochem. J.*, 1921, **15**, 620—626).—The coefficient of diffusion from normal solution into gelatin and agar gels was measured by the indicator method previously described (A., 1920, ii, 235). With increasing concentration of gel, the coefficient of diffusion at first decreases rapidly according to an exponential relation, but with concentrations above 2% the curve connecting coefficient of diffusion and concentration is approximately a straight line. It is shown how this result can be harmonised with the relation between diffusion and viscosity found by Einstein, Sutherland, and von Smolukowski. The diffusion coefficients found when extrapolated for diffusion in water are about 7·5% higher than those obtained from the results of Öholm (A., 1905, ii, 147). This is attributed to the fact that in Oholm's experiments the salt concentration refers to ionised+un-ionised salt, whereas the authors measure only the rate of penetration of the ions, which diffuse about twice as fast as the un-ionised salt.

The resistance which even a stiff jelly offers to salt diffusion is quite small; the rate is reduced by less than 2% for each gram of gelatin added to 100 c.c. when the concentration exceeds 2%.

G. B.

**Penetration of Electrolytes into Gels. IV. Diffusion of Sulphates.** WALTER STILES (*Biochem. J.*, 1921, **15**, 629—635).—In 0·5% agar, ammonium, potassium, sodium, and magnesium sulphates diffuse almost as fast as in pure water. In 10% gelatin, the rate is decreased by about 25%. The diffusion coefficient of copper sulphate in agar is considerably greater than in water, and in 10% gelatin less than in water, but still greater than the values for other sulphates indicate. The abnormal results of von Fürth and Bubanović (A., 1920, ii, 94) have not been confirmed. The comparatively small uptake of sulphates by plant tissue is not to be explained on the basis of retarded diffusion through a gel.

G. B.

**A General Theory of Solutions of Electrolytes.** JNANENDRA CHANDRA GHOSH (*Z. physikal. Chem.*, 1921, **98**, 211—238).—A theoretical paper in which the author develops a new theory of electrolyte solutions on the basis (i) that in solutions of strong electrolytes only ions exist, and (ii) in solutions of weak electrolytes or those of medium strength there exists an equilibrium between a non-polar form (non-electrolyte) and a polar form (which behaves as a strong electrolyte). This hypothesis is examined in connexion with the data obtained in recent years on electrical conductivity, activity coefficients, conductivity in non-aqueous solvents, influence of salts on solubility relations, absorption of light by salt solutions, and the relation between osmotic pressure and activity coefficients.

J. F. S.

**Theory of Strong Electrolytes.** H. KALLMANN (*Z. physikal. Chem.*, 1921, **98**, 433—437).—A number of criticisms of Ghosh's

hypothesis of solutions of electrolytes (T., 1918, **113**, 449, 627, 7( and preceding abstract) are put forward. J. F. S.

**Solubilities in Mixtures of Two Solvents.** GEORGE PUGH and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1921, **43**, 1753 1758; cf. A., 1917, ii, 445).—The solubility of forty-five orga substances has been determined at 20—25°, in ethyl alcoh quinoline, and equimolecular mixtures of the two solvents. some cases, the solubility in the mixed solvent lies either above below that in the individual solvents; this is most marked in t case of carbamide, "saccharin," *p*-nitrophenol, acetanilide, reso cinol, piperine, cinnamic acid, and chloral hydrate and in all the cases compound formation is indicated. The solubility of car amide, "saccharin," brucine, and *o*-nitrophenol in a series mixtures of alcohol and quinoline has been determined at 2 and the solubility of lactose at 1° and 25° and raffinose at 25° a series of mixtures of water and pyridine has also been determine It is shown that the solubility of carbamide decreases quite regula as the concentration of quinoline increases, but at 60% quinoli a break occurs and the compound of one molecule of quinoline a three molecules of carbamide is formed, m. p. 154°. Compou formation is indicated in the case of "saccharin," brucine, lacto and raffinose, but no definite compound was isolated. J. F. S.

**Compound Formation and Viscosity in Solutions of t Types Acid-Ester, Acid-Ketone, and Acid-Acid.** JAM KENDALL and ELIZABETH BRAKELEY (*J. Amer. Chem. Soc.*, 19 **43**, 1826—1834; cf. Kendall and Gross, this vol., ii, 32, 33). The viscosity-composition curves at 25° have been determin for the systems trichloroacetic acid–ethyl acetate, acetic aci ethyl acetate, trichloroacetic acid–ethyl benzoate, acetic aci ethyl benzoate, trichloroacetic acid–acetone, acetic acid–aceto trichloroacetic acid–acetophenone, acetic acid–acetophenone a trichloroacetic acid–acetic acid. The results obtained indica extensive compound formation in solutions of the esters and keton with a strong acid (trichloroacetic). The same substances with weak acid (acetic) give viscosity curves which are much le abnormal, although compound formation is still evident. T curve for the system acetic acid–trichloroacetic acid exhibits co siderable compound formation and an examination of the resu of previous workers on systems of the types acid–acid and acid–ba shows that this behaviour is general except when the componen are of similar acidic strength. The rules formulated in previo papers relating to the extent of compound formation with diversi in character of the components are confirmed by the present wo J. F. S.

**Compound Formation and Conductivity in Systems the Types Formic Acid–Metal Formate and Sulphuric Aci Metal Sulphate.** JAMES KENDALL, HOWARD ADLER, a ARTHUR W. DAVIDSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1846—185 cf. preceding abstract).—Electrical conductivity determinatio

have been made of solutions of various concentrations of barium, magnesium, and lead formates in anhydrous formic acid at 25°, and of solutions of sodium, barium, calcium, magnesium, zinc, lead, and silver sulphates in anhydrous sulphuric acid. In this case, the solutions contained 0·04 equivalent of solid sulphate. Comparing the results for the formates with those obtained for other formates in formic acid by Schlesinger (A., 1919, ii, 91; 1920, ii, 72, 73), it is shown that a definite parallelism exists between the degree of ionisation and the extent of compound formation. In the case of the sulphates, however, the uncertainty of the correction to be applied for the solvent is so great as to obscure the results. Variations in compound formation, solubility, and ionisation in systems of the general type $HX-RX$ are all more extreme the weaker the acidic radicle $X$. Hydroxides in aqueous solution differ more widely than formates in formic acid, and these are more diverse than sulphates in sulphuric acid solution. J. F. S.

**The Photography of Opaque Crystals.** M. François and Ch. Lormand (*Bull. Soc. chim.*, 1921, [iv], **29**, 1056—1059).—The application of the apparatus previously described for the photography of transparent crystals (cf. A., 1921, ii, 626) to the photography of opaque crystals is given in detail. W. G.

**Stereoscopic Photography of Crystals.** M. François and Ch. Lormand (*Bull. Soc. chim.*, 1921, [iv], **29**, 1059—1063).—For this purpose, a microscope, the tube of which can be inclined successively to the left and right, is used. It is fitted with the apparatus previously described for the photomicrography of crystals (cf. A., 1921, ii, 626, and preceding abstract). A photograph is taken with the tube inclined to the left and then one with it inclined equally to the right. The examination of the two photographs in a stereoscope gives a stereoscopic picture of the crystals in relief. W. G.

**Ionic Properties and Crystallo-chemical Relationships. I. The Properties of the Ions which appear in Crystals.** H. Grimm (*Z. physikal. Chem.*, 1921, **98**, 353—394).—A theoretical paper in which it is shown that the electrostatic action of the ions in crystals is due to the following ionic properties, (i) the charge of the ions, (ii) the radius of the ions, (iii) the structure of the ions, particularly the surface and number of exterior electrons. The ions are divided into five principal groups depending on the number of exterior electrons. (i) Ions of the helium type (2 exterior electrons), (ii) ions of the Ne, A, Kr, Xe, and emanation type (8 exterior electrons), (iii) ions of the $Cu^+$, $Ag^+$, $Au^+$ type (probably with 18 exterior electrons), (iv) ions of the $Te^+$ and $Pb^{++}$ type, (v) ions of the type $Mn^{++}$, $Fe^{++}$, $Co^{++}$, $Ni^{++}$ (transition ions). It is shown from many compounds and elements that the expression $\phi_A-\phi_{Ne}>\phi_{Xe}-\phi_{Kr}>\phi_{Kr}-\phi_A$ holds for many physical properties where $\phi$ is the numerical value of the property and the index is that of the inactive gas the structure of which comes nearest to that of the ion concerned. This inequality is due to an analogous inequality of the ionic radii. The ionic radii of $O^{--}$, $S^{--}$, $Se^{--}$, $Te^{--}$; $Mg^{++}$, $Ca^{++}$, $Sr^{++}$, $Ba^{++}$ have been calculated and that

of $Cs^+$ has been approximated. The series order of the other ionic radii has been deduced from the molecular volumes of isomorphous compounds in which the interchangeable ions have the same number of exterior electrons. Ions with different structures and different exterior sheaths show a similar electrostatic action when the difference in the ionic radius compensates the other properties. J. F. S.

**Structure of Organic Crystals.** SIR W. H. BRAGG (*Proc. Physical Soc.*, 1921, **34**, 33—50).—The author has determined the *X*-ray spectra of naphthalene, α-naphthylamine, benzoic acid, acenaphthene, β-naphthol, and α-naphthol by the powder method. To interpret the results, he has made the assumption that the benzene and naphthalene rings are actual structures having definite size and form, and that they are built as a whole into the organic substances in which they occur. It is shown from crystallographic and other data that this hypothesis is an extremely probable one, and it leads to results which are in excellent agreement with crystallographic data. It is shown that the unit cell of naphthalene contains two molecules aud has a mass of 213 Å.U., where 1 Å.U.= $10^{-24}$ grams, the linear dimensions of the cell are $a=8·34$, $b=6·05$, and $c=8·69$ Å.U. Two molecules of anthracene occupy the unit cell, and this has the linear dimensions $a=8·7$, $b=6·1$, and $c=11·6$ Å.U. The unit cell of acenaphthene contains four molecules, and has linear dimensions 8·32, 14·15, and 7·26 Å.U., respectively, whilst α-naphthol has a unit cell which also contains four molecules and has linear dimensions $a=13·1$, $b=4·9$, and $c=13·4$ Å.U.; the same number of molecules occupy the unit cell of β-naphthol and here the linear dimensions are $a=5·85$, $b=4·28$, and $c=8·7$ Å.U. The unit cell of α-naphthylamine also contains four molecules, and has the dimensions $a=8·62$, $b=14·08$, and $c=7·04$ Å.U. Benzoic acid has a wide spacing between the planes, the unit cell contains four molecules and has the dimensions $a=5·44$, $b=5·18$, and $c=21·8$ Å.U. In a note the author stated, "It is convenient in this work to extend the Ångstrom system of units so that an Å.U. of area is $10^{-16}$ *cm.*$^2$, *of volume* $10^{-24}$ *cm.*$^3$ *and of mass* $10^{-24}$ *grams.*" *J. F. S.*

**Röntgen Spectroscopic Investigation of Organic Compounds. I. and II.** K. BECKER and W. JANCKE (*Z. physikal. Chem.*, 1921, **99**, 242—266, 267—274).—In the first part an account is given of the *X*-ray examination of the structure of a number of organic suhstanees. The substances were examined in the form of compressed pastilles hy a method which is a comhination of that due to Bragg and Debye-Scherrer. In the case of indigotin it is found that the unit cell is an hexagonal parallelopiped with a rhombus as base of edge 19·55 Å.U. and height 11·80 Å.U. This contains 12 indigotin molecules. The figures refer to indigotin which has been subjected to a pressure of 4000—5000 atoms. Indigotin which has not been so compressed has a unit crystal cell with the linear dimensions $a=b=20·20$ Å.U., $c=12·15$ Å.U., which means that there is a volume contraction of 9·8%, the base decreases 3·2% and the height 2·9%. Carbamide has a unit cell

of dimensions $a=b=8{\cdot}75$ Å.U., $c=7{\cdot}24$ Å.U., and contains 8 molecules. The unit cell of succinic acid contains 2 molecules and has dimensions $a=5{\cdot}00$ Å.U., $b=8{\cdot}20$ Å.U., $c=5{\cdot}40$ Å.U., $\beta=94{\cdot}70°$. Compression reduces all values, the $c$ value relatively most, the values being: volume 10·3%, $a$ 2·2%, $b$ 4·8%, and $c$ 5·4%. Measurements are recorded for quinol, quinone, anthraquinone, anthracene, naphthalene, phenanthrene, resorcinol, phthalic anhydride, phthalic acid, cinnamic acid (*trans*), β-phenylpropionic acid, azobenzene, hydrazobenzene, lithium oxalate, maleic acid, succinic acid, maleic acid, *d*- and *l*-tartaric acids, pentaerythritol, α-methylglucoside, and acetylenedicarboxylic acid. The results show that the number of molecules in the unit crystal cell is always greater than one, and is not the same for nearly related substances such as maleic acid and succinic acid. In the second paper, the results of *X*-ray examination of a large number of aliphatic acids are given. The results are arranged in four groups. I. Acids with an odd number of carbon atoms, formic, propionic, valeric, heptoic, nonoic, undecoic. II. Acids with an even number of carbon atoms, acetic, butyric, octoic, lauric, myristic, palmitic, stearic (also αα′-distearin). III. Isomeric acids, *iso*butyric, *iso*valeric, trimethylacetic. IV. Unsaturated acids, crotonic, undecenoic, oleic, and elaidic. In many cases, the acids were measured as their lithium salts. It is shown in the case of the even-number saturated acids apart from the first two members that they possess an hexagon symmetry with 72 molecules in the unit crystal, or possibly rhombohedral with 24 molecules; the uneven-number acids are tetragonal with 24 or 48 molecules in the unit cell. There is no fundamental difference between the free acids and the lithium salts. J. F. S.

**Mixtures of Anisotropic Liquids and the Identity of Grandjean's Stratified Liquids with Liquids of the Azoxyphenetole Type.** G. FRIEDEL and L. ROYER (*Compt. rend.*, 1921, **173**, 1320—1322; cf. Grandjean, A., 1921, ii, 91).—In the case of mixtures of substances capable of furnishing anisotropic liquids, the two phases, the conic and thread-like (liquides à coniques et liquides à fils), are perfectly distinct and separated from one another by an absolute discontinuity. Mixtures of Grandjean's stratified liquids with other anisotropic liquids always show an absolute discontinuity between the stratified liquid and the conic phase. On the other hand, these mixtures do not show any discontinuity between the thread-like phase, and the stratified liquid of Grandjean. It is suggested, therefore, that Grandjean's stratified liquids are only a special aspect of the thread-like liquids of the type of azoxyphenetole. W. G.

**Some Fundamental Conceptions of Colloidal Chemistry.** RICHARD ZSIGMONDY (*Z. physikal. Chem.*, 1921, **98**, 14—37).—A theoretical paper in which the nature of matter in the colloidal condition is considered. The views put forward by Nägeli ("Gärung," Munich, 1879) on the nature of micellæ are considered, and it is shown that in general these views are in keeping with

experimental data. The conceptions to be generally adopted are expressed as follows: by micellæ in its broadest sense is to be understood a molecular complex of the dispersed material, which is not permeated by the dispersion medium. In the narrower sense, micellæ are crystalline, ultramicroscopic particles of the dispersed material. Micellar complexes are formed by the association of micellæ, and are ultramicroscopic particles generally, but in isolated cases may be microscopic. According to the form of the association, micellar complexes form, on the one hand, microscopic or ultramicroscopic particles which are permeated by the dispersion medium, or, on the other, ultramicroscopic or microscopic swelling crystals. J. F. S.

**An Interesting Colloid Gel.** ROSS AIKEN GORTNER and WALTER F. HOFFMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2199—2202).—Dibenzoylcystine is insoluble in water and in the crystalline state has no hydrophilic properties, but it can give rise to rigid gels which do not contain more than 0·2% of dibenzoyl-*l*-cystine. The 0·2% gel is prepared by dissolving 0·2 gram of dibenzoyl-*l*-cystine in 5 c.c. of 95% alcohol. The solution is heated and water added to make the solution up to 100 c.c. After cooling for two to three hours, the solution sets to a gel comparable with that of a 5% gelatin gel. The gel is transparent, but after several days opaque nuclei are formed, due to crystallisation, which is accompanied by syneresis, and after several weeks most of the dibenzoyl-*l*-cystine has separated in definite crystals. On applying strong suction, the liquid may be drained from the gel, thus showing the coarse dispersion. The gel has a fibrillar structure. J. F. S.

**Coagulation of Colloidal Solutions of Arsenious Sulphide by Electrolytes.** E. F. BURTON and E. D. MACINNES (*J. Physical Chem.*, 1921, **25**, 517—525).—The coagulation of solutions of arsenic sulphide sols of concentrations 0·027 gram per c.c. to 0·00337 gram per c.c. by means of potassium, lithium, magnesium, barium, aluminium, and zirconium chlorides, lanthanum sulphate, and cerium nitrate of various concentrations has been investigated. It is shown in the case of aluminium chloride that the volume of the electrolyte required for coagulation of a given amount of the disperse phase varies inversely as the concentration of the electrolyte solution, provided the final concentration of the colloid is kept constant. For univalent ions, it is shown that the concentration of ion necessary to produce coagulation increases with decreasing concentration of the colloid, whilst for bivalent ions the concentration of ion required to produce coagulation is almost constant and independent of the concentration of the colloid. With tervalent ions, the concentration of ion required to produce coagulation varies almost directly with the concentration of the colloid, whilst quadrivalent ions necessary for coagulation decrease much more rapidly than the concentration of the colloid. These results are in keeping with earlier results of Burton and Bishop (A., 1921, ii, 176). It is also shown that the coagulation curve for barium chloride shows

a tendency to resemble the curve for tervalent ions as given by aluminium chloride, whilst the curve for the quadrivalent zirconium ion differs from that of the ceric ion, which is similar to that for tervalent ions. J. F. S.

**Acidity and Basicity.** RUDOLF KELLER (*Z. physikal. Chem.*, 1921, **98**, 338—351).—A theoretical paper in which the terms acidity and basicity are considered. It is shown for the determination of the acidity of a combination solute–solvent, or the sense of the electric charge, not only the inner chemical constitution of the dissolved substance is to be considered, but also the chemical constitution of the solvent, which may, in the case of substances which are nearly amphoteric, be determinative. Further, the difference in the dielectric constants of the solvent and solute must be considered; this quantity makes its influence noticeable in the case of amphoteric, non-ionised, and associated solutes. The so-called basic dyes in aqueous solution usually migrate toward the anode, that is, they are acid according to the ruling terminology; this is particularly so in the case of the slightly dispersed and non-dissociated colour colloids; the so-called acid dyes are for the greater part basic or amphoteric. Certain acid dyes, such as picric acid, Martius-yellow, aurantia, are really acid, that is, negative, and wander to the anode. The capillary rule of Fichter-Sahlbom is generally correctly expressed in the literature, but incorrectly defined, since it places the dyes in the incorrect position in the electro-polarity series. All the experimental capillarity experiments show that immediately on dipping the paper strips, the neutral and positive dyes rise with the solvent. In this correct form, the rule holds, not only for colloids, but also for ion-dispersoids. Gobbelsröder ("Kapillaranalyse," Dresden, 1910) has actually found the strongest acids below in the anode region. The strongest acids and bases, such as hydrochloric and sulphuric acids and potassium hydroxide in suitable solvents, migrate in directions which are opposed to their nature. Concentration cells may be built up in which the strongest acids behave as bases. J. F. S.

**Homogeneity and Dispersity.** WA. OSTWALD (*Z. physikal. Chem.*, 1921, **99**, 155—159).—A theoretical paper in which the conception specific surface is investigated on the basis of the phase rule. J. F. S.

**Reactions in Heterogeneous Systems. The Systems $K_2CO_3|BaSO_4$–$K_2SO_4|BaCO_3$; $K_2CO_3|CaC_2O_4$–$K_2C_2O_4|CaCO_3$ and $K_2CrO_4|AgIO_3$–$KIO_3|AgCrO_4$.** E. RAMANN and H. SALLINGER (*Z. physikal. Chem.*, 1921, **98**, 103—150).—The systems named in the title have been experimentally investigated. By the addition by barium chloride solution to an excess of a mixture of potassium carbonate and potassium sulphate solution, the relation in which barium divides itself between the carbonate and the sulphate ions has been approximately determined. This ratio, $[CO_3'']:[SO_4'']$, is termed the precipitation equilibrium. In the

case of the addition of silver nitrate solution to an excess of the mixed solutions of potassium iodate and chromate, the original equilibrium partition of the silver takes place according to the anion ratio, $[IO_3'] : [CrO_4''/2]$, as in the previous case, but the two equilibria differ to an extraordinary degree in stability. Whilst the first can be approximately fixed by the rapid addition of alcohol, the second can only be fixed by a special experimental procedure. In the system $xK_2CO_3+yK_2C_2O_4+zCaCl_2(z<x+y)$, the precipitation equilibrium could not be fixed by the addition of alcohol. The precipitation equilibrium in general is labile, inasmuch as immediately after the precipitation a reaction is set up which brings about a change in the relationship of the salts in the solid phase and leads to the formation of one of the salts (solution equilibrium). The solution equilibrium has been determined for various concentrations for the system $K_2CO_3|BaSO_4$–$K_2SO_4|BaCO_3$; for the system $K_2CO_3|CaC_2O_4$–$K_2C_2O_4|CaCO_3$, at various total potassium salt concentrations and various temperatures and for the system $K_2CrO_4|AgIO_3$–$KIO_3|Ag_2CrO_4$ at various total salt concentrations and one temperature (20°). In the system $K_2CO_3|BaSO_4$–$K_2SO_4|BaCO_3$, the partition relationship $K_2CO_3|K_2SO_4$ shows a marked dependence on the total salt concentration. No measurements were made on the temperature influence on this ratio. In the system $K_2CO_3|CaC_2O_4$–$K_2C_2O_4|CaCO_3$, the partition relationship $K_2CO_3|K_2C_2O_4$ is but slightly influenced by the total salt concentration but very strongly influenced by temperature. The ratio $K_2CO_3|K_2C_2O_4$ is shown to be a strict linear function of the temperature. The data obtained for the systems investigated and those obtained by Knüpffer (A., 1898, ii, 420) for the system KCNS|TlCl–KCl|TlCNS and by Noyes and Kohr (A., 1903, ii, 201) for the system KOH|AgCl–KCl|AgOH have been examined by means of the formula put forward by Nernst and Noyes (A., 1891, ii, 142).
J. F. S.

**Studies on Chemical Affinity. XIII. Reaction Affinity in Systems of Solid Salts.** J. N. Brönsted (*Z. physikal. Chem.*, *1921*, **98**, *239—243*).—In earlier papers (A., 1920, ii, 290, 298), a method was described whereby the reaction affinity between very soluble solid salts might be determined. This method does not yield the required results when applied to sparingly soluble salts. In the present paper, a method is described for the determination of the reaction affinity in systems of sparingly soluble solid salts. The method has been applied to the reaction $[CoCl(NH_3)_5]Br_2+[CoBr(NH_3)_5]Cl_2 \longrightarrow [CoCl(NH_3)_5]Cl_2+[CoBr(NH_3)_5]Br_2$ and consists in determining the solubility of the four cobalt complex salts in mixtures of (i) potassium formate and chloride solution, (ii) potassium formate and bromide, (iii) sodium chlorate and chloride, and (iv) sodium chlorate and potassium bromide, where the total alkali concentration is $0{\cdot}5N$ in each case. Then from the solubility products of the four cobalt complex salts by means of the gas laws the reaction affinity may be calculated. The results of the experiments lead to the value $A_{0°}=621$ cal. for $T=273°$, a value

which is probably accurate to 1%. The system is characterised by the fact that the lighter ions are combined with the lighter ions and the heavier ions with the heavier. J. F. S.

**The Velocity of Decomposition of High Explosives in a Vacuum. III. Mercuric Fulminate.** ROBERT CROSBIE FARMER (T., 1922, **121**, 174—187).

**Sensitiveness of Very Sensitive Explosives.** J. EGGERT (*Z. Elektrochem.*, 1921, **27**, 547—558).—The sensitiveness of a number of explosives, including the iodides of nitrogen, has been experimentally investigated. The results show that the intermolecular decomposition of nitrogen iodide takes place according to the equation $8NH_3NI_3=5N_2+6NH_4I+9I_2$, whether the decomposition takes place in the dark or in light or is occasioned by detonation. Nitrogen iodide is not sensitive to shock, and many effects which were previously attributed to detonation are now shown to be secondary mechanical effects. The sensitiveness of nitrogen iodide and silver amide is not materially changed by lowering the temperature to $-190°$. Gradual isothermal increase of pressure to 5000 atm. brings about a decomposition in 70% of the cases of nitrogen iodide or silver amide, but all other explosives examined are unchanged by this treatment. An attempt is made to find an explanation of the sensitiveness of explosives; since earlier experiments have shown that the mechanical effects are not to be explained as secondary temperature effects, there only remains the possibility that local increases of pressure occur with all mechanical influences and these are to be regarded as causing the detonation. This view is supported by the present experiments on the behaviour of the sensitiveness with increase of pressure. A consideration of the processes occurring during the decomposition of explosives from the point of view of Herzfeld's theory of velocity of chemical reaction leads to a possible explanation of some of the properties of these substances. In this connexion, the primary, generally very simple, unimolecular decomposition of the explosive, which depends on the persistence of the molecule alone, is to be differentiated from the accompanying, at least bimolecular reaction, due to the collision between the products of reaction of the primary process. If in the primary reaction products are formed which possess more energy and a greater persistence than the original substances, or if, following on the primary process, other processes which are subjected to several negative accelerations occur, then there will be no marked tendency to detonation. But if, on the other hand, the primary reaction leads to the stable end products of the reaction, or if these products undergo other reactions with no retardations or at most only one retardation, then the explosive is one which has a high sensitiveness and a great tendency to detonation. Pressure is the factor which removes the retardation to the reactions, since it causes the atoms, molecules, and atomic groupings which have affinities for one another to come closer together. J. F. S.

**The Autoracemisation of Potassium Chromioxalate.** ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS (T., 1922, **121**, 196—202).

**Neutral Salt Action, at Higher Salt Concentrations; the Velocity of Hydrolysis of Ethyl Acetate, and the Hydrogen-ion Activity of the Catalyst.** GÖSTA ÅKERLÖF (*Z. physikal. Chem.*, 1921, **98**, 260—292).—The velocity of hydrolysis of ethyl acetate by $0 \cdot 05N$-solutions of hydrochloric, sulphuric, and nitric acid at 25° has been determined in the presence of various concentrations of the chlorides of ammonium, potassium, sodium, magnesium, calcium, and barium, the nitrates of ammonium, potassium, sodium, magnesium, and calcium, and the sulphates of ammonium, potassium, sodium, and magnesium. The hydrogen-ion activity of the catalyst in the various reaction mixtures has been determined by means of *E.M.F.* measurements. An attempt is made to ascertain the cause of the neutral salt action on the velocity of hydrolysis at constant acid concentration by combining the velocity measurements with the hydrogen-ion activity. A relationship between these two quantities is furnished by the formula $K=C\alpha . f(n)\sqrt[3]{\alpha}$, in which $K$ is the reaction velocity, $n$ the acid titre, and $\alpha$ the hydrogen-ion activity. The formula holds for all concentrations of catalyst, and is not influenced by the nature or concentration of the added salt, as far as the present experiments go. This formula is probably also true for the inversion of sucrose and allied reactions. The foregoing shows that the hypothesis of the catalytic activity of the non-ionised molecule is incorrect. The salt molecules have no activity of their own, but they are the cause of the change of activity of the catalyst. Exactly how the neutral salt changes the activity of the catalyst is not known with certainty, but the most probable hypothesis is that the water sheath of the hydrogen ion is changed by the addition of neutral salts. The concentration of the hydrogen ion remains constant whilst the activity changes. According to this view, the hydration numbers do not represent definite quantities, but the ions control all the water molecules in the solution. The various neutral salt actions are controlled hy the various forces with which the different ions attract the water molecules. J. F. S.

**Velocity of Hydrolysis of Acetals.** ANTON SKRABAL and ANTON SCHIFFRER (*Z. physikal. Chem.*, 1921, **99**, 290—313).—The velocity of hydrolysis of methylene dimethyl ether, methylene diethyl ether, ethylidene diethyl ether, methylene diacetate, and ethylidene diacetate has been investigated. The reactions were carried out with hydrochloric acid of various concentrations, ($0 \cdot 001 - 0 \cdot 3N$), and also in alkaline solution. It is shown that the measured velocity constants represent the velocity of hydrolysis of the first ether group; the removal of the second group is much more rapid, and is regarded as a water hydrolysis. The velocity constants vary very much for the different cases, thus for the acid hydrolysis the value of $k_a$ is 70,000 for methylene diethyl

ether, whilst for ethylidene diacetate it is 0·00650, whilst in the case of alkaline hydrolysis the value of $k$ is 1,100 for methylene diacetate and 96 for ethylidene diacetate. In the case of the hydrolysis of esters it is shown that the velocity depends largely on the nature of the acid but very little on the nature of the alcohol. These rules are established from the published data of a number of authors. J. F. S.

**Velocity of Hydrolysis of Sucrose.** R. H. CLARK (*J. Amer. Chem. Soc.*, 1921, **43**, 1759—1764).—The velocity of hydrolysis of sucrose by hydrochloric, hydrobromic, sulphuric, or nitric acid has been determined at 25°. The experiments were effected in the presence of acids of varying concentration and in the presence of potassium nitrate and dextrose. It is shown that the addition of a neutral substance, to keep the concentration of the water constant while varying the concentration of the acid, has no appreciable effect in producing a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity of sucrose. The increase in the velocity of hydrolysis of sucrose produced by a strong acid in the presence of a neutral salt of that acid over the velocity produced by the acid alone can only to a small extent be attributed to the fact that the volume of the reaction is reduced by the presence of the salt. On the assumption that both the dissociated and undissociated forms of an acid are catalytically active in sucrose inversion, the values of $K_i$ for the hydrogen ion from hydrochloric, hydrobromic, and nitric acids have the same value ($K_i$=0·234); the corresponding value for sulphuric acid is considerably lower ($K_i$=0·144). J. F. S.

**Affinity Dimensions of Weak Acids and Bases in Alcoholic Solution and the Alcoholysis of their Salts.** HEINRICH GOLDSCHMIDT, CARL GÖRBITZ, HAAKON HOUGEN, and KRISTIAN PAHLE (*Z. physikal. Chem.*, 1921, **99**, 116—154).—The theory of the alcoholysis of salts of weak acids with bases of the aniline type in anhydrous alcohol and in alcohol containing water is developed. A method of determining the degree of alcoholysis based on electrical conductivity measurements is described. The electrical conductivity of a series of sodium, aniline, and ammonium salts in pure and in aqueous alcohol has been determined. The affinity dimension of several organic acids in alcohol solution has been determined. The alcoholytic constant of eleven aniline salts has been measured and from the results the affinity constant $K_B$, corresponding with the equilibrium (Aniline × H˙)/Aniline ion, has been calculated. The same quantity has been determined for the three toluidines and mono- and di-methyl anilines. The influence of water and the alcoholytic constants has been investigated.

J. F. S.

**The Rate of Solution of Iron in Dilute Sulphuric Acid both when Stationary and under Rotation.** JOHN ALBERT NEWTON FRIEND and JOHN HORACE DENNETT (T., 1922, **121**, 41—44).

**Theory of Catalysis in Homogeneous Gas Reactions.** KARL F. HERZFELD (*Z. physikal. Chem.*, 1921, **98**, 161—174).—A theoretical paper in which an attempt is made to answer the question, "Why does a reaction proceed more rapidly through an intermediate product than by the direct action?" It is shown that since at equal concentration the slowest of all the partial reactions is determinative of the velocity of the whole process, this slowest reaction must proceed more rapidly than the original reaction when catalysis occurs. After a short review of the previously published theoretical work on gas reactions, the author considers such reactions in a way which assumes the existence of a few free atoms. Then for catalysis it is necessary that at not too small concentrations of the catalyst the heat of activation of the intermediate product (that is, practically its heat of formation from atoms) is markedly smaller than that of the starting material; in the best case about one-half. This gives then an upper limit for the acceleration which at not too high concentrations may be reached by a given catalyst. Examples on which to test the hypothesis are not known.

J. F. S.

**Catalytic Oxidation of Carbon Monoxide.** T. H. ROGERS, C. S. PIGGOT, W. H. BAHLKE, and J. M. JENNINGS (*J. Amer. Chem. Soc.*, 1921, **43**, 1973—1982).—The present work was undertaken with the object of finding a catalyst which will completely oxidise carbon monoxide at ordinary temperatures. A number of such catalysts have been prepared which cause rapid and complete oxidation. The chief of the catalysts obtained is a specially prepared manganese dioxide on which is precipitated the oxide of silver or copper or both. The silver or copper is best precipitated as the carbonate and subsequently hydrolysed to the hydroxide. The presence of water vapour limits the life of these catalysts. The decomposition temperature of silver oxide when simultaneously precipitated with calcium hydroxide is considerably lower than that of silver oxide alone. J. F. S.

**Catalytic Oxidation of Carbon Monoxide at Ordinary Temperatures.** DAVID R. MERRILL and CHARLES C. SCALIONE (*J. Amer. Chem. Soc.*, 1921, **43**, 1982—2002).—A number of catalysts for use in protective masks against carbon monoxide are described. The most successful are mixtures containing manganese dioxide and basic copper carbonate and manganese dioxide, copper oxide, cobaltic oxide, and silver oxide, respectively. These mixtures oxidise carbon monoxide rapidly and at ordinary temperatures, and, when protected by a drying agent such as calcium chloride, are suitable for use in protective masks against carbon monoxide of all concentrations below those in which an oxygen helmet would be necessary. The factors influencing activity, such as the constituents of the mixtures, the conditions of precipitation, the mechanical treatment of the precipitate, and method of drying, are discussed and a description is given of the efficiency of the mixtures under various conditions. J. F. S.

**Oxidation Catalysis. II.** L. KARCZAG (*Biochem. Z.*, 1921, **119**, 16—22).—Experiments with dyes at high dilutions show that the ferrous ion catalyses oxidation with hydrogen peroxide much faster than the ferric ion. The order of mixing is of influence, the controlling factor being whether the ferrous ion is first oxidised to ferric or not. H. K.

**Electronic Theory of the Interior of the Atom.** A. D. FOKKER (*Arch. Néerland*, 1921, **5**, [iiiA], 193—242).—A mathematical paper in which it is shown that the application of the electronic theory to the mutual actions of the electrons inside the atom gives results which are in accordance with experimental observations. J. F. S.

**Theory of Allotropy.** MAURICE COPISAROW (*J. Amer. Chem. Soc.*, 1921, **43**, 1870—1888).—Allotropy is defined as the capacity of an element to exist in forms differing in the mode of their intramolecular linking. It is therefore a function of the valency, but it does not imply isomerism or polymerism, since allotropes need not contain the same or a multiple number of atoms in their respective molecules. The number of possible forms in which an element can exist on this basis is indicated for the elements of all valencies. It is theoretically possible for an element to have in certain cases more than one molecular form corresponding with each mode of linking. Regarding allotropes as the most chemically and physically distinct forms of an element, it follows that several molecular forms, each containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element in which all atoms are rigidly fixed. Thus it follows that valency and the saturation or fixation of atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light, allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular linking. Molecular forms differing in the distribution of their intramolecular linking and in the number of atoms, but all belonging to one type of linking can be termed *allotropoids*. The allotropy of carbon, phosphorus, iron, and nickel are considered from the point of view of the hypothesis. J. F. S.

**Types of Valency.** IRVING LANGMUIR (*Science*, 1921, **54**, 59—67; cf. *ibid.*, 1921, **53**, 290; *J. Ind. Eng. Chem.*, 1920, **12**, 386, and A., 1919, ii, 328; also Rydberg, A., 1915, ii, 94).—Recognition of three distinct types of valency, (*a*) positive valency (the number of electrons an atom can give up), (*b*) negative valency (the number of electrons an atom can take up), and (*c*) co-valency (the number of pairs of electrons an atom can share with its neighbours), as well as the numerical values, for most of the elements, of each type are shown by a simpler method than that hitherto employed to be derived from certain postulates regarding the structure of atoms, and the relationships between the different types of valency are thereby further clarified. On the basis of the

Rutherford atom, only three postulates, consistent with those previously proposed, are necessary: (*a*) The electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18, and 32 electrons respectively (the extra electrons, if any, remaining in the outside layer as an incomplete layer or "sheath"). (*b*) Two atoms may be coupled together by one or more duplets (stable pairs of electrons forming the first complete layers) held in common by the completed sheaths of the atoms. A group of neutral atoms interacting by transfer of electrons gives rise to the conception of electrovalency, including positive and negative valency differing only in algebraic sign, whilst interaction by the sharing of duplets corresponds with co-valency. It is shown that the sum of the electrovalencies and co-valencies for all the atoms in any complete compound is zero, a complete compound being defined as one in which all the atoms possess complete layers of electrons. (*c*) The residual charge on each atom and on each group of atoms tends to a minimum. The term "residual charge" is employed to express the total charge of an atom or aggregate of proximate atoms regardless of sign. It is pointed out, however, that the first and third postulates are often in conflict, and that in such cases the tendency of the first may prevail against that of the third.

Chemical compounds are therefore classified according to the types of valency exhibited by their atoms as follows: (1) complete compounds, including (*a*) compounds without co-valency, such as certain simple metallic salts, volatile halogen compounds, silicates, and most minerals, and (*b*) compounds without electropositive atoms, such as organic compounds; (2) incomplete compounds, including metallic substances, and compounds such as zinc oxide, ferroso-ferric oxide, lead sulphide, and cupric oxide, which contain both electropositive and electronegative atoms; (3) exceptional cases, including nitrogen, carbon monoxide, nitric oxide, and the cyanogen radicle, the structure of which is not accounted for by this theory. These substances may have a single octet structure or possibly a triple bond structure. Other exceptions are boron hydride and certain other compounds forming double molecules.

A. A. E.

**The Expression of the Octet Theory of Valence in Structural Formulæ.** GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, **19**, 1—22).—A system for writing structural formulæ is developed, based on the octet theory of valency as presented by Langmuir.

Electronegative valence, the physical interpretation of which is vacancy for one more electron in the outer shell of the atom, is represented by a line in the usual way. Electropositive valence, on the other hand, is variable and its maximum is represented by the total number of electrons in the shell. It cannot be represented by "unsatisfied bonds" as it never causes direct union between atoms, and is expressed as follows, for example, $Na^{I}$, $Ca^{II}$. The neutral atoms having electronegative valence may satisfy that valence by acquiring an electron, that is, becoming

a negative ion; this electron may be obtained from the shell of an atom showing positive valence tendencies, and it is then left as a positive ion. These two oppositely charged ions may then form a stable compound by electrostatic attraction. Such a union is termed a salt-forming union and is expressed thus: $Na^{+}\ .\ .\ .\ .\ .\ Cl^{-}$, or $Ca^{++}\ :\ :\ :\ :\ :\ O^{--}$. On the other hand, two atoms may be held together by the shell-completing forces of both atoms acting on one or more pairs of electrons, which are then shared between them. Each shell thus fills one or more electron vacancies by sharing electrons, and thus "satisfies" one or more "bonds." This is expressed in the usual way: H—H, H—O—H, etc., and is termed a direct union. All valency relations cannot, however, be expressed in terms of either of the above unions, and a special feature of the system is the introduction of the conception of a "borrowing direct union," for cases in which both the shared electrons are supplied by the same atom. In this case, the borrowing atom fills two vacancies in its shell, and the lending atom neither gains nor loses electrons; but the union is essentially polar, since the originally neutral borrowing atom has acquired at least an interest in two negative electrons and therefore becomes a negative pole. This relationship is expressed thus:

$$\begin{array}{c}H\\H\end{array}\!\!>O\propto O,\quad \begin{array}{c}O{=}S\propto O,\\ \ \ \ \propto\\ \ \ \ O\end{array}$$

indicating that the O atom is bound to S, or to O, by virtue of having its two electron vacancies filled by borrowing an interest in two of the shell electrons of the other oxygen atom in hydrogen peroxide, and in the sulphur atom of sulphur trioxide. The mode of application of the system to all the known elements is indicated in the original paper. G. F. M.

**The Thermos Flask in the Chemical Laboratory.** CLAUDE W. BOURLET and WALTER THOMAS (*Chem. News*, **123**, 336).—The thermos flask can be utilised advantageously in the laboratory in numerous instances where it is desired to maintain substances above the normal temperature, as, for example, in reactions between liquids, or liquids and solids at elevated temperatures such as hot oxidation by permanganate and other similar reactions which are not strongly exothermic. Oil and water emulsions and similar mixtures are conveniently "split" by warming and keeping overnight in a thermos flask, and flocculent or colloidal precipitates can be dealt with in a similar manner. In carrying out certain colour tests, for example, the Halphen reaction, and reactions in media which gelatinise or become viscous at ordinary temperatures, a water-bath can with great advantage be replaced by the vacuum flask.
G. F. M.

**Water Pump.** JOHANNES WETZEL (*Chem. Ztg.*, 1921, **45**, 1122).—A water pump of improved efficiency is described; particular attention is directed to the relative diameters of the injector tube and outlet tube and to the central position of the jet as regards the outlet tube. W. P. S.

# Inorganic Chemistry.

**Separation of the Element Chlorine into Isotopes (Isotopic Elements). The Heavy Fraction from the Diffusion.** WILLIAM D. HARKINS and ANSON HAYES (*J. Amer. Chem. Soc.*, 1921, **43**, 1803—1825).—By means of elaborate diffusion a definite increase in the atomic weight of chlorine has been obtained. The increase in atomic weight amounts in different experiments to from slightly less than to considerably more than one part in a thousand (1 in 645). The diffusion experiments were effected with hydrogen chloride, and a considerable amount of the isotopic acid has been obtained. The separation of isotopes by diffusion is discussed in terms of the Rayleigh diffusion equation, which applies to the diffusion into a vacuum. It is shown that for a high efficiency the pressure of the gas on both sides of the diffusion wall should be low, first to secure good mixing, and secondly to insure that the passage through the porous partition shall be entirely molecular. A rapid and precise method for the determination of the atomic weight of isotopic chlorine has been devised. It is found that in the separation of isotopes the percentages of the different isotopes present are as important factors as the atomic weight differences. Thus, contrary to what has been supposed, it is shown, even aside from the greater difficulties involved in obtaining and handling neon, that it is easier to produce a small increase in the atomic weight of chlorine (of the magnitude of 0·05 unit) than to produce the same increase in the atomic weight of neon. J. F. S.

**Viscosities of the Hydrogen Haloids.** H. HARLE (*Proc. Roy. Soc.*, 1922, [*A*], **100**, 429—440).—The viscosity of hydrogen chloride, bromide, and iodide has been determined by the method of transpiration through a capillary tube. Measurements were made at temperatures in the neighbourhood of 20° and 100°, and from the results the viscosity is calculated for 0° and 100° respectively. The following values in *C.G.S.* units are recorded: hydrogen chloride, $\eta_0=1·332\times10^{-4}$; $\eta_{100}=1·837\times10^{-4}$; hydrogen bromide, $\eta_0=1·710\times10^{-4}$; $\eta_{100}=2·365\times10^{-4}$; hydrogen iodide, $\eta_0=1·731\times10^{-4}$, $\eta_{100}=2·403\times10^{-4}$. The values of *C*, the Sutherland constant, are 357, 375, and 390 for the three gases respectively.
J. F. S.

**Numerical Revision of the Data referring to the Density of Gaseous Hydrogen Bromide: Atomic Weight of Bromine.** E. MOLES (*J. Chim. Physique*, 1921, **19**, 135—138).—The molecular weight of gaseous hydrogen bromide with reference to oxygen has been calculated to be 80·944, and from this the atomic weight of bromine is 79·936. If, however, the value for the weight of the normal litre of oxygen recently published (cf. following abstract) is used the atomic weight of bromine becomes 79·927. J. F. S.

**Critical Study of the Modern Value of the Density of Gaseous Oxygen.** E. Moles (*J. Chim. Physique*, 1921, **19**, 100—120).—A discussion of the modern results for the density of oxygen leads to the value $L_0=1\cdot42891\pm0\cdot00003$ as the most probable value for the weight of the normal litre of oxygen. The value is deduced from 162 measurements made by nine workers using oxygen obtained from three different sources and by three essentially different methods. If only the most recent measurements by weighing a globe of the gas are considered the mean is $L_0=1\cdot42894$. Up to this the value accepted was 1·42905, which can no longer be maintained, and although the difference is only 1 in 10,000, yet it cannot be neglected in the calculation of molecular weights. It is proposed that the value 1·42891 be accepted as the standard, and this in some cases may be rounded to 1·4289. If this value is calculated to the conventional value of $g$, $g=980\cdot665$ *C.G.S.* units then the value of $L_{0N}$ becomes 1·42897, which may be rounded to 1·4290. J. F. S.

**Solubility. VII. Solubility Relations of Rhombic Sulphur.** Joel H. Hildebrand and Clarence A. Jenks (*J. Amer. Chem. Soc.*, 1921, **43**, 2172—2177).—The solubility of rhombic sulphur has been determined in carbon tetrachloride, benzene, toluene, *m*-xylene, heptane, and ethylene dichloride at 0°, 25°, 35°, 45°, and 54°. The results are expressed in molecules of $S_8$ per 100 molecules of solvent and in grams per 100 grams of solvent. The following values in grams per 100 grams of solvent are recorded: Carbon tetrachloride, 0°, 0·339; 25°, 0·831; 35°, 1·155; 45°, 1·564; and 54°, 2·008; heptane, 0°, 0·124; 25°, 0·362; 35°, 0·512; 45°, 0·698; and 54°, 0·926; toluene, 0°, 0·897; 25°, 2·018; 35°, 2·722; 45°, 3·620; and 54°, 4·85; *m*-xylene, 25°, 1·969; 45°, 3·604; benzene, 25°, 2·074; 54°, 5·165; ethylene dichloride, 25°, 0·826; 40°, 1·380; 79°, 5·43; and 97·5°, 9·97. It is shown that, with the exception of certain minor discrepancies, the solubilities of sulphur accord well with the internal pressure relations of the substances involved. J. F. S.

**The Constitution of Selenium.** H. Pélabon (*Compt. rend.*, 1921, **173**, 1466—1468).—The grey selenium previously described (cf. A., 1921, ii, 533), the specific resistance of which may vary from a few ohms to several million ohms, is now shown to consist of two modifications. The α-modification has a very high resistance and is prepared by heating selenium at a temperature only just above its melting point and then allowing it to cool slowly. The specific resistance of this modification diminishes at first very rapidly with rise in temperature and then more slowly. At 200°, the resistance is about 70,000 ohms, and at 218° the substance melts, the melting being accompanied by a sudden rise in resistance. The β-modification has a very small specific resistance. It is obtained by maintaining the molten selenium at a temperature near its boiling point for some time and then allowing it to cool. The β-modification is not stable at low temperatures, and it is

readily changed into the α-form by oscillations of its temperature between 15° and 200°. W. G.

**Influence of Freezing on Colloidal Selenium. II.** A. Gutbier, Fr. Heinrich, and J. Huber (*Kolloid Z.*, 1921, **29**, 287—293; cf. A., 1921, ii, 693).—A continuation of work previously described (*loc. cit.*) on the effect of freezing on selenium sols. Three new series of experiments are now described in which it is shown that the sensitiveness of undialysed selenium sols, prepared by means of sulphur dioxide, towards cold increases with the time during which they are frozen. The system may be frozen for short periods and will then melt to form a typical colloid, but more prolonged freezing increases the tendency to coagulate to irreversible gels on melting, and very prolonged freezing will even cause coagulation to take place in the solid. In this respect, there is no fundamental difference between dialysed and undialysed sols, but the dialysed system is somewhat more sensitive. The reducing action of sulphur dioxide on solutions of selenious acid is retarded by freezing the mixture. If the mass is kept frozen for a long time the colloid is precipitated in the ice and thereby the reduction process is accelerated. The precipitation appears to exercise a nucleus action, by which the reduction in the solid mass is accelerated, so that eventually more selenium is precipitated in the frozen mass than would be produced in a solution in the same time. In general, the coagulation in the frozen sol commences where the sol is in contact with the air, as is shown by the formation of a coloured ring on the upper surface of the ice. When test-tubes are used for the experiments, the curved lower portion of the tube always shows an increased concentration of selenium. The form of the vessel in which the freezing takes place is shown to exert an influence on the coagulation. When a sol is poured on ice and frozen it is found that the disperse phase diffuses into the ice. It has been found scarcely possible to freeze selenium sols in capillary tubes. J. F. S.

**Metallurgy of Tellurium by the Wet Way.** Pierre Hulot (*Bull. Soc. chim.*, 1921, [iv], **29**, 1070—1071).—The method of reduction of potassium anhydrotellurate by zinc and hydrochloric acid with the precipitation of metallic tellurium (cf. A., 1920, ii, 174) is modified by using aluminium and sodium or potassium hydroxide for the production of nascent hydrogen, with the result that the reduction is completed in one hour instead of ten. The aluminium must be pure and free from copper. W. G.

**Manganese in the Catalytic Oxidation of Ammonia.** Charles Snowden Piggot (*J. Amer. Chem. Soc.*, 1921, **43**, 2034—2045).—The action of manganese dioxide alone and when mixed with copper oxide or silver oxide, and various alloys of manganese, copper, silver, iron, and silica as catalysts in the oxidation of ammonia have been investigated. A mixture of manganese dioxide with 40% of copper oxide at 800° is shown to have an efficiency of more than 90%. All the substances mentioned catalyse the

oxidation of ammonia with various efficiencies which with suitable conditions are about 50%. The physical structure of the oxide catalyst is of great importance, extremely fine subdivision giving a large adsorbing surface with very small pores being conducive to greater activity. J. F. S.

**Attempt to Prepare Nitro-nitrogen Trichloride. II. Behaviour of Mixtures of Nitrogen and Chlorine in a Flaming Arc.** WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 1774—1782; cf. A., 1913, ii, 584).—Attempts to prepare nitro-nitrogen trichloride or nitrogen trichloride by passing mixtures of nitrogen and chlorine through a flaming arc were entirely unsuccessful. Passing the same gases through a powerful ozoniser had the same result and no action at all occurred with Strutt's active nitrogen. The results, although negative, confirm Lewis's hypothesis that electrons are held jointly by two atoms rather than the view that electrons are transferred from one atom to another when atoms combine. J. F. S.

**Vapour Pressures of Aqueous Solutions of Nitric Acid.** WILLIAM C. SPROESSER and GUY B. TAYLOR (*J. Amer. Chem. Soc.*, 1921, **43**, 1782—1787).—The total and partial vapour pressures of nitric acid solutions of the concentrations 20%, 40%, 56%, 68%, and 80% by weight have been measured at temperatures 0°, 35°, 50°, 65°, and 80°. From the data the vapour pressure for each 10% increase in concentration and each 10° rise in temperature has been calculated and tables drawn up. Attempts to measure the vapour pressure of 90% acid were unsuccessful owing to the decomposition of the acid at all temperatures except 0°.
J. F. S.

**Reducing Actions of Arsenious Acid.** MORITZ KOHN (*Monatsh.*, 1921, **42**, 221—226).—When copper sulphate is heated with ammonia solution and arsenious anhydride in a sealed tube in a boiling water-bath, it undergoes reduction to cuprous salt with formation of arsenic acid. After the resulting cuprous solution has been oxidised to the cupric condition by atmospheric oxygen, estimation of the arsenic acid reveals more of the latter than corresponds with the equation, $2Cu^{\cdot\cdot}+AsO_3{}'''+2OH'=H_2O+2Cu^{\cdot}+AsO_4{}'''$. Evidently oxidation of the ammoniacal cuprous solution to the cupric stage activates the atmospheric oxygen for the oxidation of the residual unchanged arsenious acid. Depression of the concentration of hydroxyl ions by addition of ammonium salts retards the reduction of cupric to cuprous salt. T. H. P.

**Catalysis in the Interaction of Carbon with Steam and with Carbon Dioxide.** HUGH STOTT TAYLOR and HARVEY A. NEVILLE (*J. Amer. Chem. Soc.*, 1921, **43**, 2055—2071).—The effect of potassium carbonate, sodium carbonate, lithium carbonate, barium carbonate, calcium carbonate, sodium chloride, ferric oxide, copper, sodium silicate, borax, and nickel as catalysts on the interaction of steam on carbon has been investigated, using various forms of

carbon. It has been discovered that the interaction of carbon and carbon dioxide is likewise accelerated by the presence of the same materials, and a striking parallelism between the catalysts for the two reactions has been shown. The probable mechanism of the steam–carbon reaction has been investigated. It has been shown that good catalysts for the water-gas reaction, for example, iron oxide, are ineffective in the steam–carbon and carbon dioxide–carbon reactions. Catalysis of the water-gas reaction thus being excluded from consideration, it has been shown that the acceleration of the reaction $C+CO_2=2CO$, and therefore the acceleration of the reaction $C+2H_2O=CO_2+2H_2$, may be ascribed to increased adsorption of carbon dioxide by the carbon surfaces in presence of active catalytic agents. Adsorption measurements confirm this view. The results have been considered in connexion with the suggested existence of a surface complex, $C_xO_y$, and have been found to agree with this conception. J. F. S.

**A Modification of Silicon Soluble in Hydrofluoric Acid.** WILHELM MANCHOT (*Ber.*, 1921, **54**, [*B*], 3107—3111).—Moissan and Siemens (A., 1904, ii, 560) have isolated specimens of silicon from a silver regulus which suffer loss of weight (up to 99%) when treated with hydrofluoric acid, and subsequently Lebeau (A., 1906, ii, 168) has brought forward evidence to show that a similar modification is present in copper–silicon alloys rich in the latter. The substance, however, does not appear to have been investigated fully.

Considerable difficulty is experienced in preparing silicon which is completely resistant towards hydrofluoric acid; the product obtained by Wöhler's method requires frequently repeated treatment with the acid before a stable specimen is secured. It is shown that an appreciable gain in weight occurs when the latter is melted with silver in an electric furnace in an atmosphere of air, oxygen, or carbon monoxide, but this is in itself insufficient to account for the subsequent solubility of the silicon. The latter, however, is only produced in the soluble condition when the regulus is suddenly cooled. The silver may be replaced by aluminium. It dissolves in hydrofluoric acid with evolution of hydrogen.

It is remarkable that Moissan and Siemens describe their product as exactly resembling crystalline silicon, whereas the author's specimens are dark to pale brown and amorphous; they leave a pale brown powder after being treated with hydrofluoric acid.

H. W.

**Organogels of Silicic Acid.** B. S. NEUHAUSEN and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1921, **43**, 1844—1846).—Hydrogels of silicic acid have been repeatedly soaked in alcohol, acetone, and benzene for long periods, dried in a vacuum of 5 mm. at 80°, 120°, and 270° successively for periods of one hour, and analysed. The dried products contain: alcogel, 4·23% water, 3·90% alcohol; acetone gel, 4·77% water, 3·75% acetone; benzene gel, 4·31% water, 3·82% benzene. Hence it follows, in opposition to Graham's

statement, that the water of a hydrogel of silicic acid cannot be entirely replaced by a second solvent. It has been previously shown that heating silicic acid gels in a vacuum at 300° for six hours does not reduce the water content below 4·8%, a quantity which is very near the amount of water left in the organo-gel above, and indicates that this water is very firmly combined in the gel.

J. F. S.

**Relative Densities of Alkali Metal Amalgams and Mercury. II.** EDGAR C. BAIN and JAMES R. WITHROW (*J. Physical Chem.*, 1921, **25**, 535—544; cf. A., 1916, ii, 431).—The methods of formation and the relative densities of liquid and solid amalgams of sodium, potassium, ammonium, and calcium have been investigated. It is shown that solid amalgams float on the mother-liquor and do not sink as stated by Kerp (A., 1898, ii, 516). The method used by Kerp (*loc. cit.*) produces sodium and potassium amalgams, which are like the amalgams produced by other methods inasmuch as the solid is lighter than the liquid. Oily and pasty amalgams are due to fine crystals incorporated in the liquid. By electrolysis of solutions of potassium chloride, amalgams with concentrations up to 2·31% of potassium were obtained. No difficulties, except those of collection and preservation, were met with in the production of ammonium amalgams by the electrolysis of solutions of ammonium chloride, but crystalline amalgams cannot be obtained in this way. Electrolysis of an acidified solution of calcium acetate is not a satisfactory method for the production of calcium amalgams, but it does produce a dilute calcium amalgam. J. F. S.

**The Production of Potassium Hydrogen Sulphate from Ammonium Hydrogen Sulphate and Potassium Sulphate.** W. DOMINIK (*Przemysl Chem.*, 1921, **5**, 10—15, 37—40, 63—67).—Reaction in the presence of steam superheated at 200—400° takes place according to the equation $M_2SO_4+NH_4HSO_4=2MHSO_4+NH_3$; lack of steam results in the production of pyrosulphates. In the above reaction, $K=[MHSO_4]^2/[M_2SO_4].[NH_4HSO_4]$ increases with the temperature according to a logarithmic function. Theoretical consideration is given to the use of a mixture of sodium and potassium sulphates in the reaction. CHEMICAL ABSTRACTS.

**Crystal Structures of Sodium Chlorate and Sodium Bromate.** ROSCOE G. DICKENSON and ELBRIDGE A. GOODHUE (*J. Amer. Chem. Soc.*, 1921, **43**, 2045—2055).—A large amount of $X$-ray spectrometer data for sodium chlorate and bromate has been obtained and tabulated. In agreement with other observers, it has been found that the nature of the crystal surface has a considerable effect on both the absolute and relative intensities of reflection. The ease with which reflections from one face may be mistaken for those from another and the necessary precautions to avoid this have been pointed out. It is shown that the atoms in sodium chlorate and sodium bromate are very

probably arranged with the symmetry of the Schönflies sp group $T^4$, all oxygen atoms being equivalent. Sets of positi of the atoms in the unit structure, only slightly different for chlorate and bromate, have been suggested. J. F. S

**Preparation and Study of the Rarer Alkali Bromat Rubidium Bromate.** HAROLD D. BUELL and C. R. McCROS (*J. Amer. Chem. Soc.*, 1921, **43**, 2031—2034).—Rubidium brom was prepared by treating the pure carbonate with an excess bromic acid and recrystallising the product (cf. A., 1920, ii, 6 The following figures are the solubilities in 100 grams of wa at various temperatures: 25°, 2·93; 30°, 3·55; 35°, 4·28, 40°, 5·08. The corresponding figures for cæsium bromate are 3·66; 30°, 4·53; 35°, 5·32. The following melting points recorded: potassium bromate, 405°; cæsium bromate, 42 rubidium bromate, 430°. Both rubidium and cæsium broma form small, cube-like crystals, which, however, belong to hexagonal system; they have a refractive index between 2· and 2·22. J. F. S

**Vapour Pressure of some Salts. II.** H. VON WARTENBE and H. SCHULZ (*Z. Elektrochem.*, 1921, **27**, 568—573; cf. Albre and Wartenberg, *ibid.*, 162).—Using the method previou employed, the authors have determined the vapour pressures lithium chloride, cæsium chloride, rubidium chloride, lithi bromide, cæsium bromide, rubidium bromide, sodium fluori potassium fluoride, lithium fluoride, cæsium fluoride, rubidi fluoride, sodium iodide, cæsium iodide, and rubidium iodi The measurements were carried in most cases up to the boil point of the salt in question. The following data are record pressures being in atmospheres: lithium chloride, b. p. 13 m. p. 606°, $\log p = -37200/4{\cdot}57T + 4{\cdot}923$; cæsium chlori b. p. 1303°, m. p. 626°, $\log p = -37400/4{\cdot}57T + 5{\cdot}190$; rubidi chloride, b. p. 1383°, m. p. 717°, $\log p = -37800/4{\cdot}57T + 4{\cdot}9$ lithium bromide, b. p. 1310°, m. p. 549°, $\log p = -35600/4{\cdot}57T$ 5·109; cæsium bromide, b. p. 1300°, m. p. 627°, $\log p$ $-36750/4{\cdot}57T + 5{\cdot}113$; rubidium bromide, b. p. 1350°, m. 681°, $\log p = -36980/4{\cdot}57T + 4{\cdot}964$; sodium fluoride, b. p. 169 m. p. 988°, $\log p = -56600/4{\cdot}57T + 6{\cdot}299$; potassium fluori b. p. 1505°, m. p. 846°, $\log p = -41900/4{\cdot}57T + 5{\cdot}138$; lithi fluoride, b. p. 1676°, m. p. 842°, $\log p = -55100/4{\cdot}57T + 6{\cdot}1$ cæsium fluoride, b. p. 1251°, m. p. 684°, $\log p = -34700/4{\cdot}57T$ 4·982; rubidium fluoride, b. p. 1410°, m. p. 775°, $\log p$ $-40000/4{\cdot}57T + 5{\cdot}243$; sodium iodide, b. p. 1300°, $\log p$ $-37000/4{\cdot}57T + 5{\cdot}130$; lithium iodide, b. p. 1170°, $\log p$ $-40300/4{\cdot}57T + 6{\cdot}105$; cæsium iodide, b. p. 1280°, $\log p$ $-36600/4{\cdot}57T + 5{\cdot}165$; and rubidium iodide, b. p. 1305°, $\log p$ $-37000/4{\cdot}57T + 5{\cdot}148$. The results show that the heats of f mation of the haloids of potassium, rubidium, and cæsium lie ve close together, whilst that of the lithium salts is much higher a that of the sodium salts much lower. J. F. S.

**Catalytic Influence of Foreign Oxides on the Decomposition of Silver Oxide, Mercuric Oxide, and Barium Peroxide.** JAMES KENDALL and FRANCIS J. FUCHS (*J. Amer. Chem. Soc.*, 1921, **43**, 2017—2031).—The effect of foreign oxides on the temperature and rate of decomposition of silver oxide, mercuric oxide, and barium peroxide under an oxygen pressure of one atmosphere has been experimentally investigated. In almost all the systems examined the added oxides ($CuO$, $MnO_2$, $Fe_2O_3$, $CeO_2$, $SiO_2$, $CrO_3$) induce a considerable change in the decomposition temperature. Most commonly, there is a marked lowering in this point; thus, quoting an extreme case, an equimolecular mixture of barium dioxide and cupric oxide has an oxygen equilibrium pressure of 1 atm. at 322°, a temperature which is approximately 500° below the decomposition temperature of pure barium dioxide. In a few systems a comparatively small rise in the decomposition temperature is indicated. In all cases, however, the rate of oxygen evolution is markedly increased. The decomposition temperatures recorded refer to true equilibrium conditions, concordant values being obtained with rising and falling temperature. The results are tentatively ascribed to the formation of unstable intermediate compounds between the two oxides present. The increased rates of decomposition may be referred to adsorption effects, but the large temperature changes point strongly to the actual participation of the added oxide in the reaction. Direct evidence was given in certain mixtures of the production of stable complexes. J. F. S.

**Physical Chemistry of the Oxides of Lead. III. Hydrated Lead Monoxide.** SAMUEL GLASSTONE (T., 1922, **121**, 58—66).

**Reactions in Fused Salt Media. I. Basic Lead Chromates.** J. F. G. HICKS (*J. Physical Chem.*, 1921, **25**, 545—560).—The reaction between lead monoxide and sodium chromate in fused sodium chloride and a 50% mixture of sodium and potassium nitrates has been investigated and the equilibrium diagram of the system $PbO-PbCrO_4$ constructed. It is shown that reactions in fused salts can be brought about in such a way as to yield products analogous to those prepared from the same initial substances in aqueous solution. The chief difference between these reactions and their analogues in aqueous solution lies in the smaller velocity of the former, probably due to the relative insolubility of the reacting substances in the fluxes as compared with water. There is in several cases a reaction between the flux and the dissolved substance, similar to hydrolysis. This analogy would appear to indicate that these solvolytic reactions are ionic, but the second phase of the reaction forming basic lead chromates points to a non-ionic reaction. It may be a purely molecular (additive) reaction, resulting in the formation of compounds of higher orders. Such a conclusion explains satisfactorily the slowness of the reactions, aside from the low solubility of the solutes in the fused salt medium. Whilst at least one basic lead chromate,

$PbO,PbCrO_4$, may be prepared by alkaline hydrolysis, it does not follow that the basic lead chromates formed in fused salt media are formed by an entirely analogous process. Two new basic chromates have been prepared by the present method which have not been obtained by the wet process; these have the formulæ, $2PbO,PbCrO_4$ and $3PbO,PbCrO_4$ respectively. A fourth compound, $PbO,2PbCrO_4$ is readily prepared by the fusion process and has been stated to be formed by the wet process, but the author has been unable to prepare it by this method. The existence of the four basic lead chromates named is confirmed by the equilibrium diagram of the system $PbO$–$PbCrO_4$. Other basic lead chromates described in the literature are shown to be mixtures or solutions of the compounds named above in one another. Salts of orthochromic acid are shown not to exist; whilst the salt $Pb_2CrO_5$ may be the salt of the monohydrate of ordinary chromic acid, it could equally well be a true basic salt or a compound of a higher order, so far as the present work is concerned. At the temperature (225—800°) the stable form of lead monoxide is yellow in colour. This, combining with yellow lead chromate yields red compounds, all of which point to compounds of a higher order. The red compound formed by alkaline hydrolysis of normal lead chromate could well be considered a basic salt, but the addition of lead oxide and lead chromate molecules to form a compound of higher order might as easily take place in aqueous solution as in the nitrate flux used to form a compound of very closely the same composition. The reddening of lead monoxide in the nitrate flux has been shown to be due to change in crystalline form, and not, as might be supposed, to the formation of red lead. J. F. S.

**Reduction of Copper Oxide by Hydrogen.** ROBERT N. PEASE and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1921, **43**, 2179—2188).—An investigation of the characteristics of the reduction of cupric oxide by hydrogen and the effect on the reaction of adding metallic copper to the oxide and water vapour and oxygen to the hydrogen has been carried out. It is pointed out that the reaction is auto-catalytic, copper being the auto-catalyst. The reaction appears to take place at the copper–copper oxide interface. This is shown by the character of the reduction curve and the fact that the addition of metallic copper accelerates the reaction. It is shown that the presence of water vapour in the hydrogen markedly interferes with the formation of the original copper nuclei from which the reaction zone, that is the copper–copper oxide interface, spreads out; it does not markedly affect the subsequent reaction at the interface, however. The presence of oxygen in the hydrogen strongly inhibits the reaction at the interface, but in all probability has no marked effect on the primary reaction, that is, the formation of the original copper nuclei.

J. F. S.

**The Oxidising Properties of Sulphur Dioxide. III. Copper Chlorides.** WILLIAM WARDLAW and FREDERICK WILLIAM PINKARD (T., 1922, **121**, 210—221).

**Behaviour of Ammoniacal and Alkaline Copper Solutions.** MORITZ KOHN (*Monatsh.*, 1921, **42**, 83—87).—When arsenic is heated in a sealed tube with ammoniacal copper solution, the cupric compound undergoes reduction, first to cuprous salt and subsequently to copper, $3Cu^{\cdot\cdot}+As+3OH'=AsO_3'''+3Cu^{\cdot}+3H^{\cdot}$ and $3Cu^{\cdot}+As+3OH'=AsO_3'''+3Cu+3H^{\cdot}$; the copper liberated unites with the excess of arsenic to form greyish-black copper arsenide. Exactly similar changes occur when antimony is heated with ammoniacal copper solutions containing tartaric acid, the solid deposited being then reddish-black and containing the copper and the excess of antimony. With bismuth and ammoniacal copper solutions containing tartaric acid, rapid action occurs, but the reduction proceeds only as far as the cuprous compound. Alkaline solutions of copper salts, such as Fehling's solution or an aqueous solution containing copper sulphate, glycerol and potassium hydroxide, are rapidly reduced by arsenic, antimony, or bismuth, with separation of copper, $2As(2Sb)+3Cu^{\cdot\cdot}+6OH'=2AsO_3(SbO_3)'''+6H^{\cdot}+3Cu$ or $2Bi+3Cu^{\cdot\cdot}=2Bi^{\cdot\cdot\cdot}+3Cu$. T. H. P.

**Separation of the Isotopes of Mercury.** J. N. BRÖNSTED and G. VON HEVESY (*Z. physikal. Chem.*, 1921, **99**, 189—206, and *Phil. Mag.*, 1922, **43**, [vi], 31—49).—A partial separation of the isotopes of mercury has been achieved by two processes. (1) Evaporation method (ideal distillation) based on the difference in the velocities of evaporation of the isotopes. The distillate was found to be richer and the remainder poorer in the lighter isotope than the original substance. (2) Effusion method. A fraction of the mercury vapour penetrates through narrow openings into a condensation chamber where the lighter isotope is found in a relatively larger amount than in ordinary mercury. The results of the experiments agree with the hypothesis, according to which the evaporation, as well as the effusion velocity of the isotopes, is inversely proportional to the square root of their molecular weights; they are further in conformity with Aston's results, obtained by means of mass spectrographic observations. The partial separation achieved was proved by measurements of density. The density difference found between the heaviest and lightest mercury amounts to 0·49%, corresponding with a difference of 0·1 unit in the atomic weight of mercury. J. F. S.

**Physico-chemical Analysis of Aluminium Oxy-salts and Aluminium Oxide Sols.** MONA ADOLF, WOLFGANG PAULI, [with FRANZ JANDRASCHITSCH] (*Kolloid Z.*, 1921, **29**, 281—287; cf. A., 1917, ii, 563; 1921, ii, 700).—The composition and nature of aluminium oxy-chloride sols have been investigated by means of measurements of the concentration of hydrogen and chlorine ions, the total chlorine concentration, and the electrical conductivity. A number of transport determinations have also been made. It is shown that it is impossible to remove all the chlorine from the products of hydrolysis of aluminium chloride by washing. A quantity of chlorine, which is greatly in excess of that contained

in the hydrochloric acid required for peptisation, always remains. On boiling well washed aluminium hydroxide with dilute hydrochloric acid, sols of various compositions are obtained up to a limiting composition represented by the formula $[Al(OH)_3]_2,AlOCl$. Of these two have been investigated. Aluminium oxy-dichloride $AlCl_2{\cdot}OH$ behaves as a ternary electrolyte and on dilution is strongly dissociated, the process being complete at a dilution 0·00106*N*. This compound shows a remarkably small hydrolysis, which amounts to 0·1% at 0·068*N*, and in a 0·00106*N* solution is only 0·25%. The compound aluminyl monochloride, $Al(OH)_2Cl$ or AlOCl, behaves as a binary electrolyte. The conductivity data indicate that a complex ionisation occurs in this case of the type $Al(OH)_2Cl|AlO$, indicating a compound in which one aluminium atom of the complex acts as the central atom of a negative complex, whilst the other furnishes a stable univalent positive ion. The peptisation of aluminium hydroxide leads to a sol of the composition $2[Al(OH)_3]Al(OH)_2Cl$, and this on dilution undergoes complex ionisation represented by the formulæ (1) $10Al(OH)_3,4AlOCl,AlO|Cl$; (2) $12Al(OH)_3,5AlOCl,AlO|Cl$; (3) $16Al(OH)_3,7AlOCl,AlO|Cl$. On the other hand, no complex ionisation of the form $Al(OH)_4|AlO$ has been observed in the case of aluminium hydroxide. J. F. S.

**Germanium. I. Extraction from Germanium-bearing Zinc Oxide. Non-occurrence in Samarskite.** L. M. DENNIS and JACOB PAPISH (*J. Amer. Chem. Soc.*, 1921, **43**, 2131—2144).—A method of extracting germanium residues obtained in the smelting of certain American zinc ores has been investigated and is described. The residue contains zinc oxide, considerable quantities of lead, arsenic, and cadmium, and small quantities of indium, tin, and antimony, in addition to the germanium. A kilogram of the crude oxide is placed in a 5-litre Pyrex flask, which is fitted with a two-holed rubber stopper carrying a bent glass tube for connexion to a Liebig condenser, and a second short glass tube for introduction of the acid. The condenser leads under the surface of water contained in a 4-litre bottle which acts as receiver. Two and a half litres of hydrochloric acid (*d* 1·18) are added to the ore and the flask is heated until 2 litres of distillate have been collected. The distillate at this point contains all the germanium and a great deal of the arsenic from the ore. The distillate is poured into a 15-litre bottle until 10 litres have been accumulated, carefully acidified with sulphuric acid until it is 6*N* (this must be carefully done to prevent loss of germanium chloride), and treated with washed hydrogen sulphide. The precipitate is at first yellow, due to arsenic, but later becomes whiter, due to the germanium. When precipitation is complete, the bottle is stoppered and kept for twenty-four hours. The solution is filtered by suction and washed with 3*N*-sulphuric acid which has previously been saturated with hydrogen sulphide. The filtrate is kept for forty-eight hours, then usually a small quantity of a white precipitate (corresponding [illegible] 2 mg. of germanium) separates, the majority of the super- [illegible] liquid is siphoned off, and the small amount of liquid and

precipitate worked up with the filtrate from the next lot of precipitate. At this point two different methods of procedure are possible.

(1) The moist sulphides are added to hot 50% sodium hydroxide until a small quantity remains undissolved; this is then just dissolved by the addition of a little more sodium hydroxide. The solution is made strongly alkaline by the addition of 8 grams of solid sodium hydroxide and placed in a large Pyrex flask fitted with a rubber stopper carrying a delivery tube, a separating funnel, and a glass tube reaching almost to the bottom of the flask. The flask is connected to a condenser and receiver as before. Washed chlorine is passed in to oxidise the arsenic to the quinquevalent condition. When the solution is saturated with chlorine, the rate of entry of the chlorine is reduced and concentrated hydrochloric acid is added in large excess from the funnel. The flask is heated until half the liquid has distilled. The germanium chloride passes over and is hydrolysed by the water in the receiver, forming white, hydrated germanium dioxide. Should oily drops form in the receiver, more water is added to reduce the acid concentration and so allow the hydrolysis to proceed. The receiver is now replaced by a second one, the distilling flask is filled up again with concentrated hydrochloric acid, and the distillation continued as before. Most of the germanium chloride passes over in the first distillation, but for a complete separation the distillation must be repeated several times. The hydrated oxide is filtered, washed first with dilute sulphuric acid and then with water, and dried at 110°. It is pure white, and contains traces of sodium, calcium, and iron, but no arsenic. The filtrates from the hydrated oxide are treated with hydrogen sulphide and the germanium sulphide is recovered. The impurities mentioned are removed by dissolving in a slight excess of sodium hydroxide, saturating with chlorine, and distilling with hydrochloric acid, hydrolysing the distillate as before.

(2) This process is generally superior to the former in its greater economy of reagents. The wet sulphides are washed with $3N$-sulphuric acid until free from chlorine and dried at 110°. They are then roasted in shallow iron dishes at temperatures not exceeding 500°. This removes a great deal of the arsenic. The roasted material is dissolved in sodium hydroxide (50%), chlorinated, and distilled with twice its weight of concentrated hydrochloric acid. A repetition of the distillation removes the last trace of arsenic. Either process gives a very pure germanium dioxide; the yield is better by the first, but the second is more rapid and economical.

Germanium in ores is estimated by grinding 20—100 grams of the finely ground, dried, and weighed ore into a paste with water and pouring into a solution of sodium hydroxide in a hard flask, the proportions being 2 of ore : 1 sodium hydroxide : 5 of water. The flask is fitted with a delivery tube for leading in chlorine, a fractionating column, and a small tap funnel. It is connected with a Liebig's condenser which leads to two Erlenmeyer flasks in series containing water to the depths of 3 cm. and half full respectively. The receivers are cooled with ice. The distilling flask is surrounded

by ice and the contents are saturated with chlorine; the solution is then neutralised by hydrochloric acid and an excess equal to twice the weight of the ore added. The ice is removed and a slow distillation in chlorine carried out until one-half the liquid in the flask has passed over. An equal volume of hydrochloric acid is added to the distilling flask and the distillation continued until its volume is again reduced by one-half. This is then repeated once more. The receivers are disconnected, acidified with sulphuric acid to make the solutions $6N$, saturated with hydrogen sulphide, and kept for twenty-four hours. In a successful experiment there will be no germanium in the second flask. The precipitate is brought on to an ashless paper and washed with $3N$-sulphuric acid, saturated with hydrogen sulphide until free from chloride, then washed with alcohol to remove the acid, and dried. The bulk of the precipitate is placed in a porcelain crucible and dried, moistened with 1 : 1 nitric acid, and warmed to drive off all the liquid, allowed to cool, treated with concentrated nitric acid, dried, and ignited. The filter-paper is incinerated in a second crucible, treated with concentrated nitric acid, and ignited. The filtrate from the germanium sulphide is kept forty-eight hours and the small precipitate formed filtered and treated as above. The weight of the germanium dioxide in the crucibles represents the germanium in the ore. Using this method, the amount of germanium in the material used for the extraction of germanium was found to be: sample I 0·247%, sample II 0·19%. Samarskite has been analysed by this method and found not to contain germanium. J. F. S.

**Crystalline Structure of Iron and Steel.** ARNE WESTGREN and AXEL E. LINDH (*Z. physikal. Chem.*, 1921, **98**, 181—210).—Various types of iron and steel have been subjected to Röntgen ray spectrographic examination. It is shown that the results of Hull (*Phys. Review*, 1917, **9**, 84, **10**, 661), that pure iron at ordinary temperatures (α-iron) possesses a space-centred cubic lattice, is in keeping with the present work. At 800—836°, that is, within the so-called β-iron region, the atoms are grouped in exactly the same way as in α-iron. Since in the authors' opinion allotropy and polymorphy are synonymous, β-iron can only be regarded as a particular modification of α-iron. In austenite and in pure iron stable at 1000°, the crystals possess a face-centred cubic lattice. This is also characteristic of γ-iron, and thereby a fundamental difference is established between α-iron and γ-iron. In martensite, the iron occurs in its α-modification. This is also the case with high speed tool steel which has been hardened at 1275°. Photomicrographs of some of the preparations examined are included in the paper. J. F. S.

**Alloys of Iron and Uranium.** E. P. POLUSHKIN (*Iron and Steel Inst., Carnegie Schol. Mem.*, 1920, **10**, 129—150; cf. *Rev. Metal.*, 1920, **17**, 421).—Alloys of iron with uranium are pyrophoric, this property varying directly with the content of uranium. Alloys containing carbon are decomposed by water, but this effect is not

exhibited by silicon, except when present in very large amount, or by vanadium. A polished sample placed on the emulsion of a photographic plate leaves an impression which, after development by the usual process, represents the structure of the specimen. Iron–uranium alloys contain the uranium carbides UC, $U_2C_3$, and $U_3C_8$, the compound $Fe_3C,U_2C_3$, as well as the compounds $V_2C$, $Fe_6U$, and FeSi. Neither uranium nor any of its compounds already mentioned forms solid solutions with iron. Vanadium has a greater affinity for uranium than for carbon. CHEMICAL ABSTRACTS.

**Equilibria in the System Fe–C–O: the Equilibrium $Fe_\beta$–Martensite–Ferrous Oxide–Gas.** W. REINDERS and P. VAN GRONINGEN (*Rec. trav. chim.*, 1921, **40**, 701—706).—A considerable number of determinations of points of univariant equilibrium for this system have been carried out. The conclusion is drawn that the transition temperature for $Fe_\beta \longrightarrow Fe_\gamma$ is 905°; this is in accord with previous results obtained by different methods. By extrapolation of the graphic results, the quintuple point of the system is found at 740° and 2300 mm. H. J. E.

**Researches on the Metallic Carbonyls.** ROBERT LUDWIG MOND and ALBERT EDWARD WALLIS (T., 1922, **121**, 29—32).

**The Action of Nitric Oxide on the Metallic Carbonyls.** ROBERT LUDWIG MOND and ALBERT EDWARD WALLIS (T., 1922, **121**, 32—35).

**Expansion of Chromium and of Nickel–Chromium Alloys over a Wide Range of Temperatures.** P. CHEVENARD (*Compt. rend.*, 1922, **174**, 109—112).—Between 0° and 100° the expansion of chromium is exactly reversible, the curve showing no singular point. The true coefficient of expansion, which is $6.8 \times 10^{-6}$ at 0°, increases rapidly with the temperature, but the curve shows a slight concavity towards the increasing temperature.

Nickel–chromium alloys containing up to 16% of chromium and from 0·5 to 2·5% of manganese were examined over the temperature range 0° to 1000°. The addition of chromium leads to a very rapid weakening of the anomaly of dilatation of nickel, and when the chromium content reaches 5% the anomaly disappears. The addition of chromium to nickel affects the expansion of this metal very little at the ordinary temperature, but tends to increase it at higher temperatures; this effect being probably due to the presence of the compound $Ni_2Cr_3$. W. G.

**Zirconium.** J. W. MARDEN and M. N. RICH (*Bur. Mines Bull.*, 1921, **186**, 146 pp.; cf. A., 1920, ii, 547).—The work is divided into four parts, dealing successively with an historical review of zirconium minerals, the salts of zirconium, and the metal; experimental work on zirconium; the furnaces used; and a bibliography of zirconium and its compounds. Analytical methods are given for the estimation of zirconium in ferrozirconium, steel, alloys such as nickel–zirconium, and a method of separation of titanium, columbium, tantalum, and zirconium. The physical and chemical

properties of amorphous and coherent zirconium are described. The cupferron method is the only one effecting complete separation of zirconium from aluminium. CHEMICAL ABSTRACTS.

**Polymorphic Transformations of Antimony Trisulphide.** SAMUEL WILSON and C. R. MCCROSKY (*J. Amer. Chem. Soc.*, 1921, **43**, 2178—2179).—The rate of transformation of the red, amorphous variety of antimony trisulphide into the black variety has been determined in the presence of *N*-, 7*N*-, 12*N*-hydrochloric acid, 7*N*-phosphoric acid, 7*N*-sulphuric acid, glacial and *N*-acetic acids, and a saturated ethereal solution of hydrochloric acid. Of these acid solutions, only the aqueous solution of hydrochloric acid gave any appreciable transformation at 18—22°, even after two months. With the aqueous hydrochloric acid, the time necessary for complete transformation was 0·5 day, 1 day, and 10·5 days for 12*N*, 7*N*, and *N*, respectively. The action is due to a solution of the red variety and a reprecipitation of the less soluble black variety. The effect of temperature was investigated with a 20% aqueous hydrochloric acid. Complete conversion at 26·5° required forty-four hours; at 30°, twenty-nine hours; 35°, sixteen hours; 40°, nine hours; 68·5°, sixty-two minutes, and 75°, thirty-two minutes. A 20% solution of hydrobromic acid gave no change after twenty hours at 75°. J. F. S.

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## Mineralogical Chemistry.

**The Ultimate Composition of British Coals.** THOMAS JAMES DRAKELEY [with FREDERICK WILLIAM SMITH] (T., 1922, **121**, 221—238).

**Kasolite, a New Radioactive Mineral.** ALFRED SCHOEP (*Compt. rend.*, 1921, **173**, 1476—1477).—This occurs together with curite (this vol., ii, 77) and torbernite at Kasolo, Katanga, Belgian Congo. It forms compact, crystalline aggregates, with sometimes tufts and radiating groups of prismatic crystals on the surface. The colour is ochre-yellow to brownish-yellow and the streak ochre-yellow. The crystals are monoclinic, with the optic axial plane perpendicular to the plane of symmetry, and the acute bisectrix of the optic axes nearly perpendicular to a perfect cleavage. $d^{17}$ 5·962, H. 4—5. Analysis I is of translucent crystals showing no sign of alteration, II of less fresh massive material, and III of clear crystals:

| | $SiO_2$. | PbO. | $UO_3$. | $H_2O$. | $Fe_2O_3$. | CaO. | MgO. | $CO_2$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 9·42 | 36·20 | 49·28 | 3·59 | 0·41 | 0·06 | 0·03 | 0·85 | 99·84 |
| II. | 9·14 | 34·44 | 49·00 | 3·77 | 0·58 | — | — | 0·53 | — |
| III. | 9·00 | 32·16 | 48·26 | 3·28 | 0·40 | — | — | — | — |

The simplest formula corresponding with the mean of these nalyses is $3PbO,3UO_3,3SiO_2,4H_2O$. The mineral is decomposed by cids with the separation of gelatinous silica and of lead chloride r sulphate. Heated in the reducing flame on charcoal it fuses to a lack glass with beads of lead. Its radioactivity is less than that f curite. L. J. S.

**Melanovanadite, a New Mineral from Peru.** WALDEMAR INDGREN (*Proc. Nat. Acad. Sci. U.S.A.*, 1921, **7**, 249—251).—his occurs as bunches of black needles on a black shale from Iinasragra, Cerro de Pasco. The crystals are monoclinic with a erfect cleavage parallel to the plane of symmetry. The streak is ark reddish-brown, $d^{15}$ 3·477, H. $2\frac{1}{2}$. Only the thinnest splinters re brown and translucent under the microscope, and the optical haracters are masked by the strong absorption. Analysis by . F. HAMILTON gives the formula $2CaO,3V_2O_5,2V_2O_4$.

| $V_2O_5$. | $V_2O_4$. | CaO. | MgO. | $Al_2O_3,Fe_2O_3$. | $SiO_2$. | Total. |
|---|---|---|---|---|---|---|
| 52·61 | 33·34 | 9·89 | 0·27 | 1·89 | 1·66 | 99·66 |

Before the blowpipe the mineral readily fuses to a brown liquid. t is readily soluble in acids, giving an apple-green solution, and in otassium hydroxide with a brown colour. L. J. S.

**Some Natural and Synthetic Melilites.** A. F. BUDDINGTON *Amer. J. Sci.*, 1922, [v], **3**, 35—87).—To test Schaller's hypothesis egarding the composition of the melilite group of minerals, comrising akermanite, gehlenite, humboldtilite, sarcolite, fuggerite, nd other varieties (A., 1916, ii, 632) more than one hundred ynthetic crystalline mixtures of $2CaO,MgO,2SiO_2$ (akermanite), $CaO,Al_2O_3,SiO_2$ (gehlenite), and $3R'O,R_2O_3,3SiO_2$ ($R'$=Ca or $Na_2$, =Fe or Al) were prepared from appropriate glasses at temeratures above 1000°. The quenching method was used (cf. erguson and Buddington, A., 1920, ii, 621), and the glasses were rystallised by annealing at a temperature just below the melting oint or the dissociation point. The homogeneity, optical charcters, and melting points were determined, and the synthetic aterials compared with the natural minerals. The gehlenite of 'elardeña consists approximately of 76% of gehlenite, 17% of kermanite, and 7% of ferric and ferrous compounds, and agrees ery closely with artificial gehlenite, having the same ratio of kermanite to gehlenite, but free from iron compounds. Other atural gehlenites examined confirm the opinion that the artificial eries of solid solutions of $2CaO,MgO,2SiO_2$ and $2CaO,Al_2O_3,SiO_2$ re pure synthetic analogues of the akermanite–gehlenite series of ninerals. Mixtures of akermanite and gehlenite form a complete eries of solid solutions with $3CaO,Al_2O_3,3SiO_2$ (grossularite) plus 0% of $3Na_2O,Al_2O_3,3SiO_2$, except for a trace of inhomogeneity in ome preparations high in akermanite. These mixtures when rystallised correspond in their properties with the humboldtilites, which are interpreted as isomorphous mixtures of positive uniaxial kermanite and a negative, uniaxial, tetragonal, moderately birefringent form of grossularite, with minor amounts of gehlenite, a

ferrous compound, and $3R'O,R_2O_3,3SiO_2$ compounds. The compositions of the humboldtilites lie in a zone which exhibits the lowest temperatures of complete melting for the components involved. Artificial crystalline mixtures containing ferric iron ($3CaO,Fe_2O_3,3SiO_2$) were fonnd to be quite different from the natural melilites of similar composition rich in ferric iron. The latter probably were formed at temperatures lower than those of the present experiments, since some of them were found to decompose or invert at temperatures as low as 850°. A new specimen of melilite rich in ferric iron, from Capo di Bove, differs in composition from any hitherto known. It contains:

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. | $Na_2O$. | $K_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|
| 40·03 | 5·66 | 7·76 | 0·4 | 9·43 | 32·17 | 2·83 | 1·72 | 100·0 |

The crystals have a tabular or pseudo-cubic habit and are intimately associated with nephelite and pyroxene. E. H. R.

## Analytical Chemistry.

**The Graphical Representation of the Composition of Chemical Compounds.** JULIUS HÜBSCHER (*Chem. Ztg.*, 1922, **46**, 19—20).—The repeated calculation of the percentage of the various constituents of chemical compounds in mixtures can be avoided by calculating once and for all the percentage of the required constituent (for example, anhydrous sodium carbonate in the decahydrate) and dividing a vertical line in these proportions. A square is then described with this line as its right-hand side and the points marked off joined to the left-hand top corner. From this co-ordinate system the weight of any constituent corresponding with a given weight of any other constituent can be rapidly read off with sufficient accuracy for practical purposes. Should the given weights not lie between 0 and 100 they can be divided by a suitable factor and the corresponding weight read off the diagram and subsequently multiplied by the same factor. H. C. R.

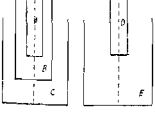
**The Sensitiveness of Coloured Indicators at Temperatures above the Ordinary.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1921, **40**, 775—785; cf. Schoorl, A., 1907, ii, 388).—Indicators which are themselves weak acids are almost all as sensitive to hydrogen ions at higher temperatures as at ordinary temperatures. Those which are weak bases become less sensitive to hydrogen ions, but retain the same sensitiveness to hydroxyl ions. Theoretical deduction of these facts is given in addition to experimental evidence. The suggestion is made that the results obtained may be of service in providing a colorimetric method of studying variations in dissocia-

tion constant and of hydrolysis constant with change of temperature and may also be of use in analytical work. H. J. E.

**Further Elaboration of the Indicator Method without Buffers.** L. MICHAELIS and R. KRÜGER (*Biochem. Z.*, 1921, **119**, 306—327).—The salt error and temperature coefficient of *m*-nitrophenol have been determined, and a new one-colour indicator, 2 : 5-dinitrophenol, described. A theoretical and practical treatment of the effect on the $P_H$ of a solution of the addition of an indicator is given, and instructions for the colorimetric estimation of $P_H$ in solutions weak in buffers, for example, sea and river waters. A discussion of the theory of the salt-error and of the activity theory of ions is also given. H. K.

**A Stable Single Buffer Solution, $p_H$ 1 to $p_H$ 12.** S. F. ACREE, R. R. MELLON, PAULINE M. AVERY, and E. A. SLAGLE (*J. Infect. Dis.*, 1921, **29**, 7—10).—The components of the buffer solution are: (1) One mol. of potassium dihydrogen phosphate, with dissociation constant, $K_a$ $1{\cdot}1\times10^{-2}$; (2) 0·625 mol. of sodium formate, $K_a$ $2\times10^{-4}$; (3) 0·375 mol. of sodium acetate, $K_a$ $2\times10^{-5}$; (4) the second group of dipotassium hydrogen phosphate, $K_a$ $2\times10^{-7}$; (5) 1 mol. of sodium phenolsulphonate, $K_a$ $10^{-10}$ (approx.); (6) 0·005 molar thymol to saturation (for water, 0·08), $K_a$ $0{\cdot}5\times10^{-10}$ (approx.); (7) the third group of phosphoric acid, $K_a$ $10^{-12}$. A curve is given from which the amounts of 0·5 molar hydrogen chloride or sodium hydroxide necessary to produce a given $p_H$ may be directly determined. CHEMICAL ABSTRACTS.

**Colour Standards for the Colorimetric Measurement of Hydrogen-ion Concentration.** LOUIS J. GILLESPIE (*J. Bact.*, 1921, **6**, 399—405).—The recently published studies of Medalia are in disagreement with other published data (cf. *ibid.*, 1920, **5**, 441—468). A colorimeter for two-coloured indicators is described for the measurement of the hydrogen-iou exponent of indicators. The optical assumptions underlying its use are practically the same as those on which ordinary colorimetry are based. The instrument is used as follows.




The glass vessels *A* and *C* are fixed in position, and *B* can be moved up and down, the motion being measured by a pointer (not shown) fixed to *B* and moving on a scale divided into 100 parts. The pointer moves from 0 to 100 when *B* moves from contact with *C* to contact with *A*. The acidified indicator solution may be placed in *B* and the alkaline indicator solution of the same strength in *C*. *A* is left empty. If the scale reads 70, the path of light along the left dotted line passes through the alkaline form of the indicator for 10% of its path and the acid form for 30%. The light along the right-hand dotted line traverses an indicator solution in tube *E*, again of the same strength, and over a path equal in length to the total path on the left. The

solution, the $p_H$ of which is unknown, is placed in tube $E$, in whicl titrations may be made. CHEMICAL ABSTRACTS.

**A New Apparatus for Colorimetric Estimations.** O MANNEBACH (*Chem. Ztg.*, 1922, **46**, 20).—The apparatus consist of a wooden box open at the top the inside of which is painte black. Into this fits a glass vessel filled with water. The botton of the box has a hole cut in it allowing light to come up throug the glass vessel, and below is a rotating frame carrying a dead white porcelain plate. The solutions to be compared are placed i glass tubes 16 mm. in diameter and 300 mm. long, which are place in the glass vessel in a slanting position. The apparatus is suitabl for the colorimetric estimation of carbon in iron. H. C. R.

**A Gas Receiver of Convenient and Practical Form fo Sampling Expired Air for Analysis.** CHARLES CLAUD GUTHRIE (*J. Biol. Chem.*, 1921, **48**, 373—378).—Whilst less efficier than the mercury receiver, the apparatus described has the advantag of being inexpensive. Expired air, after storage in it for som hours, gave results, on analysis, with an error of about 1% f carbon dioxide and considerably less for oxygen. E. S.

**Apparatus for Estimation of the Gases in Blood and Othe Solutions.** DONALD D. VAN SLYKE (*Proc. Nat. Acad. Sci.*, 192 **7**, 229—231).—Essentially a much simplified form of the apparat described in A., 1917, ii, 422, and this vol., ii, 78. The upp part of a large pipette (for instance, 50 c.c.) ends in a tap funne The stem above the wide portion has a mark, indicating a defini volume $a$ from there to the tap (for instance, 2 c.c.), and belo the wide portion another mark indicating a volume $A$ (for instanc 50 c.c.) from it to the tap. The pipette is joined below to a tul of 800 mm. connected with an open manometer and through tap, with a mercury reservoir. A definite volume of solution (f instance, 1 c.c. of blood) is sucked in through the tap funnel ar then the necessary reagent (for instance, acid for a carbona solution), making a total solution of $S$ c.c. (for instance, 2·5 c. and the mercury is allowed to fall to the lower mark. The low tap is closed, and the pipette is shaken for one to two minutes establish equilibrium. Mercury is then let in through the low tap until the gas volume is $a$ c.c. and the pressure is read ($m$ mm The zero point is then determined by expelling the gases or aft absorbing one or more of them by introducing small, measur volumes of gas-free absorbent solutions. The pressure is th lowered until the space above the solution is again $a$ c.c. and re ($n$ mm.). The volume at $N.T.P.$ of the gas given off $V=a(m-n)/760 \cdot \{273/T+S\alpha/(A-S)\}$. The term $S\alpha/(A-S)$, which $\alpha$ is the volume of the gas dissolved in 1 c.c. of the solution $N.T.P.$ corrects for the portion of the gas remaining dissolved wh equilibrium is reached. It is negligible for oxygen and nitrogen, b not for carbon dioxide. The solubility of the latter gas also impos an empirical correction for reabsorption of the gas while undergoi reduction from 50–$S$ to $a$ c.c. With $S$=50 c.c. $a$= 2 c.c. the fact is 1·020, that is 2% of the carbon dioxide is reabsorbed. G. B.

**The Use of Mercuric Nitrate instead of Silver Nitrate in ıe Estimation of the Halogens.** I. M. Kolthoff and Ada ık (*Chem. Weekblad*, 1922, **19**, 14—16).—The method proposed r Votoček (A., 1918, ii, 238, 272, 330), in which mercuric nitrate used with sodium nitroprusside as indicator, gives very accurate sults for chlorides (and for bromides, cyanides, and thiocyanates) a correction is applied for the excess of mercuric salt necessary produce a precipitate under given conditions of composition ıd volume of solution. Tables of corrections are given. Neither lute acids nor the common metals (except copper, cobalt, nickel, ıd cadmium) interfere. The method estimates accurately chlorides conductivity water, and gives good results for as little as 9 mg. chlorine per litre; it is suitable for the estimation of chlorides urine. S. I. L.

**Use of Perchloric Acid as an Aid to Digestion in the jeldahl Nitrogen Estimation.** Brainerd Mears and obert E. Hussey (*J. Ind. Eng. Chem.*, 1921, **13**, 1054—1056).—ı the estimation of nitrogen in such substances as milk, urine, ısein, gelatin, dried blood, etc., by the Kjeldahl method, the time quired for the digestion with sulphuric acid is reduced to about venty minutes if perchloric acid is added to the mixture. For ıch gram of sample, 25 c.c. of sulphuric acid, 1 gram of copper ılphate, and 2 c.c. of 60% perchloric acid should be used, but ıe presence of an excess of perchloric acid causes loss of nitrogen. W. P. S.

**Micro-Kipp Apparatus for the Preparation of Air-free arbon Dioxide for Use in the Micro-estimation of Nitrogen y Pregl's Method.** A. Schoeller (*Z. angew. Chem.*, 1921, 4, 586).—The apparatus consists of two small cylindrical bulbs, ne above the other; the upper one contains fused potassium-odium carbonate and is provided with a tapped delivery tube, hilst a side tube on the lower bulb connects with an upper acid eservoir. The apparatus is made all in one piece. W. P. S.

**Estimation of Very Small Quantities of Arsenic in Silicate ocks.** O. Hackl (*Chem. Ztg.*, 1921, **45**, 1169).—Ten grams of ıe finely-powdered sample are heated at 250° in a tube through hich a current of dry carbon dioxide saturated with bromine apour is passed; the outlet end of the tube is connected with a eceiver containing 10 c.c. of dilute nitric acid and the receiver ıay be connected with a vessel containing sodium hydroxide olution to absorb the excess of bromine. The contents of the eceiver are subsequently evaporated with the addition of a small uantity of sulphuric acid, the residue is dissolved in water, and he arsenic in this solution estimated by the Gutzeit method. W. P. S.

**Method for Direct Estimation of Carbon Dioxide and xygen in the Berthelot Bomb and its Importance for the Metabolic Balance of Herbivora.** W. Klein and Maria Teuber (*Biochem. Z.*, 1921, **120**, 81—89).—An extension of the

work of Zuntz and co-workers on the use of the Berthelot bomb calorimeter for the analysis of organic substances, the main feature now introduced being the determination of the oxygen used, by weighing. It may prove useful for the analysis of the metabolic excreta of herbivora. H. K.

**Micro-elementary Analysis by Pregl's Method.** A. SCHOELLER (*Z. angew. Chem.*, 1921, **34**, 581—583).—A short review of tbe method, with a detailed description of the apparatus used. W. P. S.

**Simplified Construction of the Metal Parts of the Apparatus used in Pregl's Micro-analytical Method.** A. SCHOELLER (*Z. angew. Chem.*, 1921, **34**, 587).—Convenient methods of attaching the heating apparatus for the lead peroxide, the micro-burner, the drying chamber, etc., to the stand are described, the parts being provided with brass rods which fit into a boss on the stand. W. P. S.

**Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis.** G. L. KELLEY and E. W. EVERS (*J. Ind. Eng. Chem.*, 1921, **13**, 1052).—Powdered sodium hydroxide, which will pass through a 5-mesh sieve but be retained on a 20-mesh sieve yields satisfactory results when used to absorb carbon dioxide in the estimation of carbon. W. P. S.

**The Separation of Silver from Mercurous Salts.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1680—1683).—The treatment of the mixed chlorides precipitated in Group I with ammonia will not separate small quantities of silver from mercurous chloride. A better method is to treat the mixed chlorides, after exhaustive washing with boiling water to remove lead, with 2% potassium cyanide solution. Silver and mercuric cyanides dissolve in the reagent, whilst black metallic mercury is precipitated. After filtering, silver is again precipitated by means of hydrochloric acid; mercuric chloride remains in solution, and may be detected after filtering, by means of sodium sulphide. The test detects 0·05 mg. of silver in presence of 50 mg. of mercurous mercury and will also detect 0·5 part of mercury in presence of 100 parts of silver. S. I. L.

**The Titration of Zinc.** E. MONASCH (*Pharm. Weekblad*, 1921 **58**, 1652—1656).—The thiocyanate method of Kolthoff and van Dijk (*ibid.*, 538) has been applied to the estimation of zinc in alloys The potassium mercuric thiocyanate solution is prepared by dissolving 23·7 grams of mercuric thiocyanate in a concentrated aqueous solution of 14·4 grams of potassium thiocyanate, and is stable for many months. Compounds of all the common metals interfere, but ferric and aluminium salts do not affect the reaction Since the author uses aluminium in the separation of zinc from alloys, the method is suitable for the estimations, but iron salts must first be oxidised by means of peroxide. S. I. L.

**Estimation of Minute Amounts of Lead in Water, with Notes on certain Causes of Error.** D. Avery, A. J. Hemingway, V. G. Anderson, and T. A. Read (*Proc. Austral. Inst. Min. Met.*, 1921, 173—199).—By the following method it is possible to detect and estimate with considerable accuracy 1 part of lead in 100,000,000 parts of water. A known volume of the water is filtered, and 2·5 to 5 litres of the filtrate are evaporated to about 100 c.c., just neutralised with hydrochloric acid, and 2 c.c. excess of acid are added, the liquid is filtered and the filtrate cooled and made up to 250 c.c. Hydrogen sulphide is passed into the solution for one hour and, after remaining over-night, the precipitate, which is usually barely visible, is collected and washed with cold water containing hydrogen sulphide in solution. Two portions of 2 c.c. of hot nitric acid (*d* 1·2) are then successively poured over the filter to dissolve the sulphides, and the filter is washed with hot water. The filtrate is evaporated with 1 c.c. of sulphuric acid until the latter fumes strongly, and the liquid, after cooling, is treated with 20 c.c. of cold water and 10 c.c. of absolute alcohol, and the mixture set aside over-night. The precipitated lead sulphate is collected and washed with a mixture of 65 vols. of water, 32 vols. of absolute alcohol, and 3 vols. of sulphuric acid. It is dissolved off the paper by dropping successively two portions of 5 c.c. of hot 33% ammonium acetate solution round the edges and then washing the paper thoroughly with hot water. The solution is transferred to a 50 c.c. Nessler tube and treated with 1 c.c. of 10% potassium cyanide solution, 1 c.c. of ammonia solution, and six drops of freshly-prepared ammonium sulphide solution. Into the standard tube are placed the same reagents in the same quantities; the liquid, which must be absolutely colourless, is diluted to 45 c.c., and a standard solution of lead acetate (1 c.c.=0·00001 gram of lead) is added until the tint matches that of the assay. If more than 8 c.c. of the standard are required, a proportionately smaller quantity of the sample should be used. To estimate the lead in the sediment, it is evaporated to dryness with hydrochloric acid, the residue is taken up with 2 c.c. of the same acid, the solution filtered, and the assay finished in a similar way to that of the water.

The estimation of lead in urine is carried out by evaporating 1 litre of the sample with 50 c.c. of nitric acid to dryness, first on a water-bath, then on the hot-plate. The dish is then placed in a cool, electrically heated muffle and gradually heated to 450—500° to destroy organic matter and nitrates. The residue is dissolved in water, the liquid just neutralised with hydrochloric acid, 2 c.c. more acid are added, and the solution is filtered. The filtrate is treated for lead as described above.

All the materials used in the above work should be redistilled from lead-free glass apparatus, the ammonium acetate should be made by neutralising freshly distilled ammonia with acetic acid, and the ammonium sulphide must be made immediately before use. All filter-papers before use must be washed with hot dilute hydrochloric acid, hot ammonium acetate solution, and hot water

successively to remove the minute amounts of lead introduced by the acid washing process of rendering them ashless. A blank test must be made, using the same quantity of redistilled water as that used for the assay and putting it through the whole of the operations. A. R. P.

**New Method for the Volumetric Estimation of Copper.** S. MINOVICI and AL. IONESCU (*Bul. Soc. Chim. România*, 1921, **3**, 89—93).—The salt $CuSO_4,4NH_3$ is quite stable at the ordinary temperature, and is quantitatively precipitated from aqueous solution by addition of eight volumes of 98% alcohol. The precipitate, after thorough washing with alcohol, is redissolved in water, and titrated with *N*/10-sulphuric or oxalic acid, with methyl-red as indicator. J. K.

**Rapid Estimation of Mercury in Ores.** ALFRED HEINZELMANN (*Chem. Ztg.*, 1921, **45**, 1226—1227).—The author has made comparative tests on the estimation of mercury in ores, using a modification of Whitton's method (*U.S. Bureau of Mines, Bull.* 78, 1918) which consists in heating the ore with a mixture of 3 grams of fine iron filings and 3 grams of good lime and collecting the mercury on a cooled silver plate previously weighed, and his own method (A., 1921, ii, 521) and finds that both methods give equally satisfactory results. [Cf. *J. Soc. Chem. Ind.*, 1922, 61A.]
A. R. P.

**The Analysis of Aluminium Alloys.** H. MENDE (*Chem. Ztg.*, 1922, **46**, 49—50).—One gram of the alloy is heated with 5 c.c. of water and 12 c.c. of strong potassium hydroxide solution (the latter added gradually) on a water-bath until nothing further dissolves. The liquid is diluted with water, the clear liquor decanted through a small filter-paper, and the precipitate washed by decantation, first with dilute potassium hydroxide solution, then with hot water. The filter-paper is burnt in a platinum spiral, the ash added to the metallic residue in the beaker, and the whole dissolved in 5 c.c. of strong nitric acid and 15 c.c. of water; 75 c.c of water are added, the liquid is boiled and the precipitate collected, washed, ignited, and weighed as tin dioxide. It should be tested for traces of silica. The filtrate is evaporated with 5 c.c. of sulphuric acid until the latter fumes strongly, the mass is treated with 150 c.c. of water, and the precipitated lead sulphate estimated in the usual way. The filtrate is electrolysed with a current of 0·5 ampere at 2·0—2·2 volts for one and a half hours at 75°, using a spiral anode and a gauze cathode. The gain in weight of the latter represents copper. The solution is neutralised with sodium hydroxide after adding any zinc found by treating the potassium hydroxide solution of the alloy with sodium sulphide, and 50 c.c. of a 50% solution of sodium hydroxide are added in excess. The solution is again electrolysed, using the same anode and cathode (the latter being coppered or silvered) for two to three hours at 70°, using a current of 1—1·5 amperes at 4 volts. The gain in weight cathode represents zinc. Silicon is estimated in a separate

trial in which 3 grams of the alloy are evaporated with 50 c.c. of a mixture of 2 parts of sulphuric acid, 3 parts of hydrochloric acid, 1 part of nitric acid, and 4 parts of water. After the metal has dissolved, the solution is evaporated with 30 c.c. of strong sulphuric acid until the latter fumes strongly, the liquid is treated with 300 c.c. of water, and the silica, which separates in an easily filterable, flocculent form, is collected, washed, ignited, and weighed as usual. Iron is determined by treating 3 grams of the alloy in potassium hydroxide solution, collecting the insoluble residue, and dissolving it, after thorough washing, in nitric acid. The solution is evaporated to dryness, the nitric acid destroyed by evaporation with hydrochloric acid, the copper and heavy metals are removed by hydrogen sulphide, the iron is precipitated from the oxidised solution by ammonia, redissolved in acid, reprecipitated as before, and the final precipitate either weighed as $Fe_2O_3$ after ignition, or dissolved in sulphuric acid, reduced, and titrated in the usual way.

For the estimation of traces of iron in pure aluminium, 3 grams of the metal are heated with 50 c.c. of strong potassium hydroxide solution, 200 c.c. of 50% sulphuric acid are added, the solution is heated until everything has dissolved, then quickly cooled, and titrated with *N*/10-potassium permanganate. Copper and silicon are estimated as described above for alloys. A. R. P.

**Germanium. II. Identification of Germanium by its Visible Arc Spectrum.** JACOB PAPISH (*Chem. News*, 1922, **124**, 3).—Photographs of the arc spectrum of germanium were obtained by means of a Hilger constant deviation spectrograph fitted with a flint glass prism ($n_D$=1·7537), the arc being made between carbon electrodes, the lower positive one carrying the material to be tested. Under these conditions, the little-known germanium line in the blue, λ 4686, is very sharp and intense, and very suitable for the identification of the metal. The line overlaps the prominent zirconium line of wave-length 4688.

G. F. M.

**The Carrying Down of Calcium Oxide by Precipitates of Ferric Oxide.** A. CHARRIOU (*Compt. rend.*, 1921, **173**, 1360—1362; cf. Toporescu, A., 1920, ii, 450).—In order to get the minimum co-precipitation of calcium hydroxide with ferric hydroxide, the concentration of the calcium salt should be as small as possible and the minimum amount of ammonium hydroxide requisite for the precipitation of the ferric hydroxide should be used. W. G.

**Estimation of Nickel in Steels.** H. RUBRICIUS (*Chem. Ztg.*, 1922, **46**, 26).—From 2 to 5 grams of the borings are dissolved in 40—80 c.c. of nitric acid (*d* 1·2), and the solution is cooled and treated with 250 c.c. of ammonia (*d* 0·91). It is transferred to a graduated flask and diluted to 500 c.c. of which 250 c.c. are filtered through a dry paper, diluted to 500 c.c., and the solution, heated at 40°, is treated with 20—30 c.c. of a 1% alcoholic solution of dimethylglyoxime. After half an hour the precipitate is filtered

on a 15 cm. paper, washed with hot water, dried, and ignited to nickelous oxide in a platinum crucible and weighed. 0·7858× NiO=Ni. A. R. P.

**Estimation of Chromium in Ferrochromium by Electrometric Titration.** G. L. KELLEY and J. A. WILEY (*J. Ind. Eng. Chem.*, 1921, **13**, 1053—1054).—Twenty grams of sodium carbonate are fused in a nickel crucible and then cooled, the crucible being rotated during the cooling so that the carbonate forms a lining. A mixture of 16 grams of sodium peroxide and 1 gram of the sample is then fused for three minutes in this crucible, the heat being so regulated that the sodium carbonate lining is not fused; when cold, the contents of the crucible are dissolved in 300 c.c. of water, the solution is boiled for thirty minutes, cooled, 80 c.c. of sulphuric acid (*d* 1·58) are added, the solution is boiled for a further five minutes, cooled, filtered, and the filtrate diluted to 1 litre. One hundred c.c. of this solution are treated with 25 c.c. of sulphuric acid and titrated with ferrous ammonium sulphate solution, using the apparatus described previously by the authors and Adams (A., 1917, ii, 512). W. P. S.

**Tungsten.** HERBERT LAVERS (*Proc. Austral. Inst. Min. Met.*, 1921, 101—152).—The paper contains a short description of the chemistry and metallurgy of tungsten together with a summary of the various processes that have been described for the estimation of tungsten in low grade ores. A volumetric method is recommended in which the tungsten is precipitated with cinchonine hydrochloride from acid solutions, and the precipitate dissolved in ammonium acetate, an excess of lead acetate added, and the excess determined by titration with ammonium molybdate. [Cf. *J. Soc. Chem. Ind.*, 1922, Feb.] A. R. P.

**Estimation of Thorium in Monazite Sand by an Emanation Method.** HOMER H. HELMICK (*J. Amer. Chem. Soc.*, 1921, **43**, 2003—2014).—A method of estimating thorium in monazite sand is described. The sample is sieved through a 40 per cm. mesh and dried at 115—120°. Two grams are well mixed with 5 grams of potassium hydrogen fluoride and 5 grams of anhydrous, recently fused, metaphosphoric acid, and slowly brought to the highest temperature obtainable with a Méker burner in a 35 c.c. platinum crucible. A further 5 grams of metaphosphoric acid are slowly added during the heating; when the mass is clear, it is allowed to cool. After cooling, 20 c.c. of 80% orthophosphoric acid are added, and the crucible is heated in an air-bath at 250—255° for three hours, the solution being automatically stirred with a platinum wire; in this way a viscous solution is obtained. A small vessel made of glass and fitted with a ground stopper and inlet and outlet tubes is suspended in a vessel of concentrated sulphuric acid at 190—200° and the liquid from the crucible poured in. The solution vessel is removed from the acid, allowed to cool, and the remaining contents of the crucible are washed in with two quantities of 20 c.c. of water, the total volume made up to 75 c.c.,

and the vessel closed in an air-tight manner. The electroscope measurements are made, (i) with a blank, prepared in exactly the same way as the sample except that the monazite is omitted, (ii) with a standard solution containing a known amount of thorium, and (iii) with the sample solution. The percentage of thorium is calculated by means of the expression $X=AT_s(T_b-T_u)/T_s(T_b-T_s)$ in which $X$ is the percentage of thorium in the sample, $A$ the percentage in the standard, $T_s$ the time of discharge of the electroscope by the standard, $T_b$ by the blank, and $T_u$ by the sample under investigation. The main sources of error of Cartledge's emanation method (A., 1919, ii, 120) were adsorption of thorium $X$ by suspended matter in final solutions, by filters, and by the walls of the vessels used. These errors are avoided in the present method by producing a complete solution of the sand without filtration and in a single vessel. Other improvements made use of are a highly efficient form of vessel to contain the solution during de-emanation; the use of an automatic regulator to maintain constant pressure in the ionisation chamber during measurements; maintenance of optimum pressure gradient along the air current line through the measuring apparatus, thus assuring a minimum error on account of pressure variations, and maximum speed of measurement; protection of the insulation of the electroscope by means of a current of dry air. Analyses by this method gave results agreeing very well with results obtained by gravimetric methods, and required much less time for each determination.

J. F. S.

**Detection of Bismuth in Urine.** PIERRE AUBRY (*J. Pharm. Chim.*, 1922, [vii], **25**, 15—18).—Following the administration of bismuth salts the metal is at least to some extent eliminated in the urine. In certain cases, it manifested its presence as a black precipitate of bismuth sulphide, but in other cases no precipitation occurred, and the metal was detected by evaporating to dryness, calcining the residue, dissolving the ash in hot dilute nitric acid, and adding a reagent containing 1% of quinine sulphate and 2% of potassium iodide dissolved in slightly acidified water, which produces an orange-red coloration or precipitate, according to the amount of bismuth present. This reagent is sufficiently sensitive to detect 1 part of $Bi_2O_3$ in 600000 parts of water. G. F. M.

**Estimation of Alcohols by Acetylation.** H. WOLFF (*Chem. Umschau*, 1922, **29**, 2—3).—The acetylation is carried out by weighing out 0·5 gram of the sample in a test-tube 0·6—0·8 cm. wide and 10 cm. long. One c.c. of acetic anhydride is added and the tube sealed, the lower end being kept in cold water the while. The tube is heated for one hour in a boiling water-bath, removed, and allowed to cool. It is then placed in a well-stoppered, thick-walled flask, and broken by vigorous shaking. The stopper is bound on and the flask heated at about 50° for half an hour on the water-bath with constant shaking, cooled, and neutralised to phenolphthalein. Twenty-five c.c. of $N/2$-alcoholic potash are

added and enough alcohol to make a clear solution. The flask is either left over-night or warmed for a quarter to half an hour at 50—60°, cooled, and titrated back with $N/2$-acid. The results obtained are within less than 1% of the theoretical. Solvents such as light petroleum or benzene have no effect on the result. If esters are present, their saponification value must be allowed for. H. C. R.

**New Methods of Blood Sugar Estimation. Estimation of the True Sugar Content of Urine.** D. G. COHEN-TERVAERT (*Nederl. Tijdschr. v. Geneesk.*, 1921, **65**, ii, 857—864, 3065—3069).—I. The methods of Schaffer and Hartmann (A., 1921, ii, 417), Folin and Wu (A., 1919, ii, 308), and of Ponder and Howie (A., 1921, ii, 417) deserve full recommendation. The first-named has been worked out for 0·1—0·2 c.c. of blood.

II. Sumner's method (A., 1921, ii, 564) has been compared with a fermentation method due to Nagasaki (*Nederl. Tijdschr. v. Geneesk.*, 1915, ii, 1478) and found to be very accurate. A few small modifications were introduced. G. B.

**A Source of Error in Testing Urine for Dextrose with *o*-Nitrophenylpropiolic Acid.** GEORGES RODILLON (*J. Pharm. Chim.*, 1922, **25**, 56—57).—Dextrose is not the only reducing agent likely to be found in urine which will reduce *o*-nitrophenylpropiolic acid to indigotin. The presence of hydrogen sulphide will both show this reaction and give a positive result in the sodium nitroprusside reaction for acetone. It does not reduce Fehling's solution. If the tests are carried out after clarifying the sample with lead acetate, these misleading results are avoided. H. C. R.

**The Identification of Lævulose in Presence of Aldoses.** I. M. KOLTHOFF (*Chem. Weekblad*, 1922, **19**, 1—2).—To 2 c.c. of the 1% sugar solution are added in succession 4 c.c. of $N/10$-iodine solution and 5 c.c. of $2N$-sodium hydroxide. This order of addition must not be reversed. The mixture after shaking is left for one to one and a half hours and the excess of iodine removed by addition of a few drops of $N$-thiosulphate. Two c.c. of Fehling's solution No. II and 2 c.c. of Fehling's solution No. I are added, the tube is shaken, and warmed in a boiling water-bath for not more than five minutes. A red coloration in one minute shows 5% fructose in presence of glucose; in two minutes, 2½%, and in four minutes 1% of fructose. After five minutes, glucose alone gives the red colour.

The test detects 0·2 mg. of lævulose in presence of 10 mg. of dextrose, 10 mg. of sucrose, and 10 mg. of lactose. S. I. L.

**Estimation of Sugar by Titration with Alkali of the Cuprous Oxide Precipitated from Fehling's Solution.** A. HANAK (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 248—250).—The cuprous oxide obtained from the inverted sugar solution containing not more than 0·5% of invert-sugar, and 50 c.c. of Fehling's solution is washed, dissolved in aqua regia, diluted to 250—300 c.c. with water free from carbon dioxide, and carefully neutralised with

sodium hydroxide so that it gives a pale greenish-yellow colour with methyl-orange. Phenolphthalein is added and $N/2$-sodium hydroxide run in until the red colour remains for three minutes in the boiling solution. One c.c. of $N/2$-sodium hydroxide = 0·0159 gram of copper. H. C. R.

**Detection of Traces of Lactose in Urine by Formation of Formaldehyde.** KURT HERZBERG (*Biochem. Z.*, 1921, **119**, 81—92).—The injection of lactose for testing the functioning capacity of the kidney necessitates a ready method for its recognition in urine. Concentrations of 0·2% can be recognised by isolation of the osazone, oxidation of the latter with permanganate to formaldehyde which can be detected by a colour test, for example, the reaction with peptone and ferric chloride. H. K.

**Polarisation of Normal Sucrose Solution.** VLAD. STANĚK (*Z. Zuckerind. čechoslov.*, 1921, **45**, 417—423; 425—431).—After correction for water, ash, invert-sugar, error of the polarimeter, etc., a normal solution of sucrose (recrystallised) polarised 99·9° Ventzke, using a dichromate filter, or 100·1° Ventzke, when a filter was not used. W. P. S.

**Use of Invertase for Sucrose Estimation.** T. SWANN HARDING (*Sugar*, 1921, **23**, 546—547).—Errors in acid hydrolysis of sucrose by the Clerget method include the hydrolysis of other sugars present and the effect of the acidity on optical non-sugars. Using invertase, no effect is found on compounds present other than sucrose. Invertase can be obtained of sufficient strength to invert a 10% sucrose solution in two hours. The activity of invertase may be retained for a year and a half.

CHEMICAL ABSTRACTS.

**Detection of Fatty Acids by the Formation of their Sodium Uranyl Salts.** J. BARLOT and (MLLE) M. T. BRENET (*Compt. rend.*, 1922, **174**, 114—116).—Streng's reaction for the microchemical detection of sodium (cf. *Ber. oberhess. Ges. Nat. Heilkunde*, 1883, **22**) based on the formation of a characteristic crystalline precipitate of sodium uranyl acetate with uranyl acetate in the presence of acetic acid, gives positive results if acetic acid is replaced by its homologues in which there is an even number of carbon atoms in the straight chain. In the case of derivatives of acetic acid, the reaction depends on the nature of the substituent. The chloroacetic acids do not give the reaction, but sodium phenylacetate and uranyl nitrate give, at once, crystals of the double salt, $CH_2Ph{\cdot}CO_2Na,(CH_2Ph{\cdot}CO_2)_2UO_2$. W. G.

[**Estimation of Arachidic Acid.**] J. PRITZKER and R. JUNGKUNZ (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 232—241).—See this vol., i, 208.

**A rapid Method for Determining the Acetyl Value of Oils and Fats.** ALEXANDRE LEYS (*J. Pharm. Chim.*, 1922, **25**, 49—56).—The following values are determined: the saponification

value $S$ of the oil or fat, the saponification value $S'$ of the acetylated oil or fat and the ratio $K$ between the weight of the acetylated matter and that of the oil or fat from which it has been prepared. The acety value $A$ is given by $A=S'-S/K$. To determine $K$, a weighed quantity of the oil or fat is boiled with ten times its volume o acetic anhydride under a reflux condenser for two hours, cooled diluted with benzene, and transferred to a tared dish. The benzene and excess of acetic anhydride are evaporated on a water-bath and the acetylated oil or fat is weighed. The acetyl value of an oil or fat dissolved in a neutral solvent having no acetyl value may be obtained without evaporating off the solvent as follows One weighed portion ($P'$) of the mixture is acetylated and the excess of acetic anhydride removed as above. The saponification value $S'$ of this is then obtained. A further portion is saponified without acetylating, giving a saponification value $S$. $S'-S=A$ represents the quantity of potassium hydroxide required to neutralise the acetic acid which has combined with 1 gram of th mixture. This has increased its weight by $42\times A_0/56=0\cdot75\,A_0$ Therefore $P'$ grams of fat has become $P''=P'(1+0\cdot75\,A_0)$ gram of acetylated fat. A saponification value $S''$ can therefore b calculated, based on the weight of acetylated oil or fat. Th acetyl value $A=S''-S/K$. H. C. R.

**Detection of Vegetable Oils in Animal Fats. The Phytosteryl Acetate Test.** C. F. Muttelet (*Ann. Falsif.*, 1921, **14** 327—333).—The cholesteryl acetate obtained from butter, lard or beef fat (by treating the fatty acids at 70° with alcoholi digitonin solution, collecting the precipitated compound, con verting it into the acetate and recrystallising the latter twice from alcohol) has m. p. 114·0° to 114·3°, whilst the phytosteryl acetat obtained in a similar way from coconut oil or earthnut (arachis oil has m. p. 124·5° to 126·5°. This method will detect the presenc of 10% of vegetable oil in an animal fat. W. P. S.

**Presence and Estimation in the Total Lipoid Ether soluble Phosphorus of Phosphorus Compounds other tha Phosphatides.** (Mlle) Eliane Le Breton (*Bull. Soc. Chim Biol.*, 1921, **3**, 539—546).—The ordinary indirect method estimating lecithins as ether-soluble phosphorus is subject to a error, unless the material is purified by precipitation with aceton according to MacLean (A., 1914, i, 1197). About 20% of impuriti remain in the acetone, which contains free and combined glycer as well as phosphorus. These impurities are not formed b hydrolysis of lecithin during extraction. G. B.

**Titrimetric and Spectrometric Analysis of Keto-En Mixtures.** Karl von Auwers and Helene Jacobsen (*Annale* 1922, **426**, 161—236).—The general plan of the series of research of which this paper forms a part has already been fully describ (A., 1918, ii, 381), and it is now shown that by following the meth of computation previously indicated spectrochemical data m be employed to estimate with moderate certainty the proporti

enol in a keto-enol mixture. It is true that the method breaks ›wn in certain cases owing to the difficulty of estimating the ›tical constants for one or other of the pure constituents; K. H. ›yer's titration method also gives somewhat uncertain values particular cases. However, when the indications of both ›thods are definite they are in remarkably good agreement.

The following substances have been examined. The percentages present the enol-content estimated spectrochemically, whilst e figures in brackets are the values determined by titration with omine: ethyl acetylmalonate, 70% (69); ethyl propionyl›lonate, 43% (44); ethyl *n*-butyrylmalonate, 55% (55); ethyl ›butyrylmalonate, 47% (47); ethyl *iso*valerylmalonate, 57% 5); ethyl hydroxymethylenemalonate, 100% (94); ethyl droxymethylene-ethyl ketone, ?% (<100); hydroxymethyle*cyclo*hexanone, assumed 100% (100); 3-methyl-6-hydroxy›thylene*cyclo*hexanone, <100% (91%); 3 : 4-dimethyl-6-hydroxy›thylene*cyclo*hexanone, ?% (89); hydroxymethylenementhone, % (97); acetylacetone, 82% (84); propionylacetone, 76% (72); ›thylacetylacetone, 33% (36); ethylacetylacetone, 31% (29); opylacetylacetone, 31% (32); benzoylacetone, 100% (100); opionylacetophenone, 93% (94); butyrylacetophenone, 88% )); *iso*valerylacetophenone, 89% (85); methylbenzoylacetone, % (9); methyl benzoylacetate, 20% (19); ethyl benzoylacetate, % (21); ethyl α-benzoyl-*n*-butyrate, 2% (4). C. K. I.

**Colour Reactions of Phenacetin and Acetanilide.** L. ›KERT (*Pharm. Zentr.-h.*, 1921, **62**, 735—737).—Under definite nditions, phenacetin and acetanilide give different colorations ›en hydrolysed with sulphuric acid and then oxidised with tassium dichromate. If 0·1 gram of phenacetin is boiled for one nute with 5 c.c. of 10% sulphuric acid, the solution then cooled, uted to 5 c.c., and treated with 2 drops of 1% potassium ›hromate solution, a violet-red or red coloration is obtained. etanilide under similar treatment, but when boiled for two nutes, yields gradually a greenish-blue coloration. W. P. S.

**Alkalimetric Estimation of Amino-acids and Peptides.** CHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 21, **54**, [*B*], 2988—2993).—The acid of ammonium salts can be imated alkalimetrically with phenolphthalein as indicator if › aqueous solution of the salt is mixed with a sufficient amount alcohol, since ammonia does not affect the indicator in alcoholic ution. It is essential that the solution should contain about % of alcohol and that relatively much indicator should be used. nino-acids and polypeptides show a similar behaviour. Characteric differences are shown, however, in the concentration of the ›ohol which is necessary for the elimination of the action of the ›ino-groups or of hydroxyl ions. The polypeptides, peptones, d proteins behave in the same manner as the ordinary carboxylic ›ds in solutions containing 40% of alcohol, whereas amino-acids the aliphatic series or of aliphatic character require an alcoholic

concentration of about 97% to produce this effect. Ethyl alcohol can be replaced by propyl alcohol, which appears to be even more effective, but not by methyl alcohol. The behaviour enables amino-acids and polypeptides to be estimated simply in mixtures of the substances by titrating with alkali hydroxide solution to neutrality towards phenolphthalein in 50% and 97% alcoholic solution. If $a$ and $b$ are the volumes of alkali solution used, the proportion, $x$, required by the amino-acids (since the majority of the latter and, in any case, those which predominate in the general mixtures neutralise in 50% alcoholic solution 28% of the amount required for complete neutralisation) is $100(b-a)/72$ and the proportion used by the polypeptides is $b-x$. H. W.

**Estimation of Urea.** F. MEZGER (*Pharm. Zentr.-h.*, 1921, **62**, 719—721).—A simple gasometric method is described. One c.c. of the urine is placed in a small tube and this in turn is placed in a reaction bottle containing 30 c.c. of hypobromite solution and connected with the top of a burette; the latter is filled with water to the zero point by means of a levelling reservoir and serves as a measuring vessel for the nitrogen evolved when the urine and hypobromite solution are mixed. A definite volume (for example, 1 c.c.) of 2% urea solution is treated in the same way and at the same time in an exactly similar apparatus. This is taken as the standard and the amount of urea in the urine is calculated from the ratio of the two volumes of nitrogen obtained. W. P. S.

**Quantitative Gravimetric Micro-analysis of Urea. Application to the Estimation of Urea in 1 c.c. of Blood.** MAURICE NICLOUX and GEORGES WELTER (*Compt. rend.*, 1921, **173**, 1490—1493).—The use of Fosse's xanthydrol reagent (cf. A., 1914, i, 859; ii, 506) is combined with Pregl's micro-methods of analysis (cf. *Die quantitative organische Mikroanalyse*, Berlin, 1917). To 1 c.c. of solution containing not more than 0·2 mg. of urea are added 1 c.c. of glacial acetic acid and 0·2 c.c. of 5% xanthydrol solution in methyl alcohol. The mixture is stirred, and after thirty minutes the precipitate is collected in a Neubauer micro-crucible and washed alternately with saturated solutions of xanthylcarbamide in alcohol and water and finally with two drops of distilled water. The precipitate is dried at 105—110° and weighed on a micro-balance. For the estimation of urea in serum, 1·0 c.c. or 0·5 c.c. is used. It is diluted with exactly five times its volume of water, and a volume of Tanret's reagent equal to the original volume of the serum is added. After five minutes the precipitate is filtered off and, in 1 c.c. of the filtrate, the urea is precipitated as above. The weight of xanthylcarbamide obtained is thus just equal to the weight of urea present in 1 c.c. of the original serum.
W. G.

**Estimation of Uric Acid in Blood.** CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1922, [vii], **25**, 5—15).—The following modus operandi is recommended for the colorimetric estimation of uric

acid in blood: The blood or serum is first freed from albuminous substances by mixing 4 c.c. with 4 c.c. of 10% sodium tungstate solution, 28 c.c. of distilled water, and 4 c.c. of 2·7% sulphuric acid, shaking vigorously, and filtering until a clear filtrate is obtained. For ordinary clinical work, the uric acid may then be estimated directly in the filtrate by adding to 20 c.c. 1·5 c.c. of 40% solution of crystallised sodium carbonate, 0·5 c.c. of the sodium phosphotungstate reagent, and sufficient water to make 25 c.c.; and comparing in a colorimeter with a standard sulphite solution of uric acid prepared according to the directions of Folin and Wu (A., 1919, ii, 308). For a more exact estimation, it is preferable to separate the uric acid from the dealbuminised blood by means of silver lactate as described by Folin (*loc. cit.*). This separation of the uric acid is, however, always necessary if working with a solution containing red corpuscles, and by so doing it was demonstrated that blood usually contains a slightly lesser quantity of uric acid than serum. The author does not favour the dealbuminisation of the blood by Grigaut's method, using 20% trichloroacetic acid. G. F. M.

**Detection and Estimation of Morphine and Other Alkaloids in Animal Excreta and Organs.** CURT WACHTEL (*Biochem. Z.*, 1921, **120**, 265—283).—Previous methods for the estimation of morphine in animal tissues are very laborious and time-consuming. A new process is described which takes about one and a half days. Urine is submitted to a preliminary purification by basic lead acetate and the morphine, in the lead-free filtrate, precipitated by phosphotungstic acid in weakly acid solution. The washed precipitate is decomposed in alkaline solution by sodium potassium tartrate and the morphine, in solution, oxidised to $\psi$-morphine by an excess of a standard solution of potassium ferricyanide. The excess of the latter is estimated iodometrically. When the morphine is present in tissues a preliminary extraction is made by means of acidified alcohol. The extract from brain and muscle in addition to purification by basic lead acetate has to be submitted to a further purification by boiling with copper sulphate, the copper-free filtrate being then precipitated with phosphotungstic acid. The process is applicable to other alkaloids provided they are not adsorbed by the basic lead acetate precipitate. H. K.

**The Bliss Method for the Separation of Strychnine from Quinine.** L. E. WARREN and A. H. CLARK (*J. Amer. Pharm. Assoc.*, 1920, **10**, 267—270; cf. A., 1920, ii, 276).—The method is shown to be untrustworthy. The quinine fractions invariably contained strychnine. In most cases the strychnine fraction was comparatively free from quinine so that the method may have a qualitative value in detecting the presence of strychnine in mixtures. CHEMICAL ABSTRACTS.

**The Estimation of Proteins in Blood—a Micro-method.** PAUL E. HOWE (*J. Biol. Chem.*, 1921, **49**, 109—113).—The author

uses 0·5 c.c. of blood and the micro-Kjeldahl method. For the *fibrinogen and non-protein nitrogen*, he follows the technique of Cullen and Van Slyke (A., 1920, ii, 398). For the rest, the method indicated in the following abstract. G. B.

**The Use of Sodium Sulphate as the Globulin Precipitant in the Estimation of Proteins in Blood.** PAUL E. HOWE (*J. Biol. Chem.*, 1921, **49**, 93—107).—In order to apply the Kjeldahl method more readily, the author substitutes sodium sulphate for the ammonium salt. At 37°, critical zones in the precipitation are observed when 13·5, 17·4, and 21·5% of sodium sulphate are present in solution. These correspond respectively with the precipitation of euglobulin (as usually separated by carbon dioxide or saturated sodium chloride) and of that of two $\psi$-globulins I and II. G. B.

**Reaction for Blood with Hydrogen Peroxide in statu nascendi.** A. PATZAUER (*Chem. Ztg.*, 1921, **45**, 1056).—A small quantity of magnesium peroxide is dissolved in very dilute acetic acid and, when violent evolution of gas ceases, guaiacum tincture or benzidine dissolved in acetic acid is added, followed by the ethereal extract of the blood. W. P. S.

**Measuring Soil Toxicity, Acidity, and Basicity.** R. H. CARR (*J. Ind. Eng. Chem.*, 1921, **13**, 931—933).—The *acidity* or basicity of a soil and the amount of soluble iron and aluminium in the same may be estimated as follows: 50 grams of the soil are shaken for two minutes with 30 c.c. of a saturated solution of potassium thiocyanate in 95% alcohol; if, after settling, the liquid has a red colour, $N/10$-alcoholic potassium hydroxide solution is added until the colour disappears. Each c.c. of the alkali solution required is equivalent to 200 lbs. of calcium carbonate per acre. Should a red colour not appear on the addition of the thiocyanate, the mixture is titrated with $N/10$-alcoholic hydrochloric acid until a pink coloration is obtained. The relative amount of aluminium in solution is indicated by the depth of the blue colour produced when the thiocyanate extract of the soil is treated with a few drops of logwood tincture. Soluble iron and aluminium salts seem to be toxic to plants. W. P. S.

**The Estimation of Tannin in Wines.** PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1087—1088; cf. A., 1912, ii, 612).—A reply to Clarens (cf. A., 1921, ii, 719). W. G.

# General and Physical Chemistry.

**Visible Refraction and Dispersion in Aqueous Solutions of Salts, particularly Coloured Salts.** G. LIMANN (*Z. Physik*, 1921, **8**, 13—19).—The refractive indices for the *D*, $H_\alpha$, $H_\beta$, and $H_\gamma$ lines have been measured for 0·3, 0·5, 1·0, 2·0, and 4·0*N* solutions of ferrous chloride, bromide and nitrate, copper nitrate and chlorate, ferric chloride, manganous chloride, bromide and nitrate; nickel chloride, bromide, nitrate and chlorate, cobalt chloride, bromide, nitrate and chlorate, aluminium chloride and nitrate; potassium chromate, dichromate, ferrocyanide and ferricyanide, chromic chloride and bromide, lithium sulphate, chromate and dichromate, magnesium chromate, cæsium bromide and nitrate, glucinum chloride and nitrate, mercuric chloride, lead nitrate, and sodium chromate. Two constants are deduced from the measurements by means of which the refraction of a solution may be calculated if the equivalent conductivity for the particular concentration is known. The influence of temperature on the refraction and dispersion has been determined in the case of potassium bromide over the range 6—30°. The results show that the dispersion decreases markedly with decrease of temperature, but the refraction is not much influenced. Thus over the measured range of temperature the refraction changes only 1/1500 for a change of 1°.

J. F. S.

**Eisenlohr's Refractometric Constants.** WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, **1**, 104—115).—A theoretical paper in which the author attempts to prove the constancy of atomic refraction of the atoms of organic substances. An analysis of the experimental data leads the author to the conclusion that the method employed by Brühl and Eisenlohr is not a rational method. This method of determination of the atomic refraction, based on the calculations of the mean value obtained from a large number of compounds, only serves to cancel the individual differences of the compounds investigated. The author has used a different method. For the calculation of the atomic refractions he takes the molecular refractions of the eight compounds, pentane, *iso*pentane, hexane, octane, di*iso*butyl, di*iso*amyl, *cyclo*hexane, and *cyclo*pentane, and has calculated the most probable mean value of the refractivity of the group $CH_2$, $\zeta_{CH_2}$, and that of hydrogen, $\zeta_H$, by the method of least squares, the equations employed being of the type $M_D = n\zeta_{CH_2} + 2\zeta_H + \Sigma\Delta\zeta$, and $M'_D = n\zeta_{CH_2} + \Sigma\Delta\zeta$. In the solution of the equations, it is assumed that the increment $\Sigma\Delta\zeta = 0$. The values thus obtained are compared with those of Eisenlohr, $\zeta_O =$ (2·418) 2·490, $\zeta_H =$ (1·100) 1·066 $\zeta_{CH_2} =$ (4·618) 4·622, Eisenlohr's values being bracketed. The results show an agreement for the value of $\zeta_{CH_2}$, but a difference of about 3% for $\zeta_H$. In the case of compounds containing oxygen, the equation $M_D = n\zeta_{CH_2} + \zeta_O + \Sigma\Delta\zeta$ is used. The figures obtained show considerable deviations of the

value $\Sigma\Delta\zeta$, that is to say, this increment cannot be regarded as zero. Similar results are obtained for both alcohols and ethers. The agreement obtained on comparing the author's value with those of Eisenlohr is explained by the dominant rôle of $n\zeta_{CH_2}$ and the insignificant influence of $\Sigma\zeta_x$, which corresponds with a residual refraction of the molecule in the equation $M_D=n\zeta_{CH_2}+\Sigma\zeta_x+\Sigma\Delta\zeta$. The author concludes that the methods employed by Brühl and Eisenlohr to determine the atomic refractivity mask the variability of this quantity and scarcely give any real knowledge of the refraction of the atoms. J. F. S.

**Molecular Coefficients of Refraction.** K. VON AUWERS and H. KOLLIGS (*Ber.*, 1921, **55**, [*B*], 21—45).—In recent publications, Eisenlohr (A., 1920, ii, 717; 1921, ii, 1, 229) has pointed out that the "molecular coefficient of refraction" $M\times n_D^{20}$ is more sensitive to constitutive changes than the generally employed molecular refraction, and has calculated values for aliphatic, benzenoid, and polymethylene compounds; this work is now exhaustively criticised.

A protest is raised against Eisenlohr's method of deriving corrected values. Thus in the case of the *cyclo*hexane series, he has assumed that the *E* values for the hydrocarbons may be derived from those of the corresponding, analogously constituted, alcohols and ketones by the deduction of 0·35. This rule is not fulfilled by 1-methyl*cyclo*hexan-4-ol or 1-methyl*cyclo*hexan-4-one, and the values for these substances have therefore been recalculated from the relationships that are supposed to exist among position-isomeric *cyclo*hexane derivatives. It is shown, however, that these recalculated values lead to data for the refractive index which differ so widely from the experimental values that the latter could only have been obtained by the use of grossly impure material and that this assumption is devoid of experimental basis.

The work on the benzenoid hydrocarbons has been examined in detail. In correcting the observed values for the refractive index to a temperature of 20°, Eisenlohr has preferred the factor 0·00065 or 0·00060 for each degree to the generally employed factor 0·00045. An exhaustive survey shows that this is generally unjustifiable. In the cases of benzene, toluene, and, to a less extent, of ethylbenzene, the higher factor is to be preferred, but in the cases of seventeen other hydrocarbons it is shown experimentally that the lower factor is in very close agreement with the observations. Since the bulk of Eisenlohr's data for the constants of aromatic hydrocarbons are based on von Auwers's observations which have been regarded as erroneous when they do not harmonise with the theory, the values have been redetermined with more particular reference to *m*-ethyltoluene, *m*-propyltoluene, *p*-ethyltoluene, *p*-propyltoluene, and *p*-diethylbenzene. The previous specimens were obtained by the reduction of the corresponding ketones by Clemmensen's method. The latter are prepared by the Friedel-Crafts method and also according to the scheme $C_6H_4MeBr \longrightarrow C_6H_4Me{\cdot}CHMe{\cdot}OH \longrightarrow C_6H_4Me{\cdot}COMe$, and the

physical constants of the products obtained in either manner are found to be identical. The constants of the hydrocarbons obtained by their reduction are in good harmony with those observed previously. A second method of preparation consists in replacing the hydroxyl group of the carbinols, $C_6H_4Me{\cdot}CHR{\cdot}OH$, by bromine and reduction of the bromides by sodium in the presence of moist ether; the indices of refraction of these preparations are mostly lower than those of the first group, practical identity being encountered only with *p*-propyltoluene. Thirdly, the Fittig synthesis is employed which gives specimens having refractive indices lower by 0·002—0·003 than those of the Clemmensen preparations. The discrepancies are far beyond the limits of experimental error. It appears impossible to decide which preparations have the greater claim to purity, since, on the one hand, the Clemmensen products are generally obtained smoothly and in good yield, whereas the "Fittig" specimens, although isolated from more complex mixtures, have constants which harmonise better with Eisenlohr's rules.

Examination of the new data obtained for the benzenoid hydrocarbons in accordance with Eisenlohr's principles leads the author to the following conclusions. Ortho-derivatives can be easily recognised by the markedly higher refractive coefficient, but this does not represent any advance, since it has been shown previously that they are differentiated so sharply from their position isomerides by density, refractive index, and specific exaltation that any of these factors is alone suitable for this purpose. The older methods do not allow the distinction between meta- and para-compounds and in this respect Eisenlohr's constant appears also to be useless; thus in the cases of *m*- and *p*-xylene the refractive indices do not differ by more than one part in a thousand parts and this position is not improved by multiplying them by their molecular weights. Position isomeric tri-derivatives are easily distinguished from one another by their different molecular refractive coefficients, but this was easily possible previously. The relationships of substances with four side chains cannot yet be elucidated.

The molecular coefficient of refraction cannot replace the spectrochemical constants, particularly the specific exaltation, but can only serve as an amplification of them. If it is desired to assign a substance to a particular group or to elucidate the general character of a group of substances, the most trustworthy data are to be derived from the specific exaltation, since in this the influence of homology or position isomerism is but little noticeable. When, on the other hand, it is desired to elucidate questions of structure within a group of substances, the molecular refractive coefficients are likely to be extremely valuable.

The following new data are recorded. Benzene, $n_D^{20}$ 1·50092. Toluene, $n_D^{19.9}$ 1·49653, $n_D^{20}$ 1·49647. Ethylbenzene, $n_D^{20}$ 1·49606. Propylbenzene, $n_D^{20}$ 1·49241. *iso*Propylbenzene, $n_D^{20}$ 1·49199. *m*-Xylene, $n_D^{20}$ 1·49782. *p*-Xylene, $n_D^{19.9}$ 1·49685, $n_D^{20}$ 1·49680. 1-Methyl-2-ethylbenzene, $n_D^{20}$ 1·50381. 1-Methyl-2-propylbenzene, $n_D^{20}$ 1·49931. *o*-Cymene, $n_D^{22}$ 1·501, $n_D^{20}$ 1·50188. *p*-Cymene (from camphor), $n_D^{20.2}$

1·48885, whence $n_D^{20}$ 1·48894 (from cymene-*p*-sulphonic acid), $n_D^{24·1}$ 1·48942, whence $n_D^{20}$ 1·49122. *p*-Diethylbenzene, $n_D^{20}$ 1·49671. ψ-Cumene, $n_D^{19·9}$ 1·50527, whence $n_D^{20}$ 1·50523. Mesitylene, $n_D^{20}$ 1·49981. Prehnitol, $n_D^{20}$ 1·51865. Ethyl-ψ-cumene, $n_D^{15·75}$ 1·51047, whence $n_D^{20}$ 1·50856. 1 : 3 : 5-Methyl-2-ethylbenzene, $n_D^{20}$ 1·51167. *m*-Tolylmethylcarbinol (from magnesium *m*-tolyl bromide and acetaldehyde), b. p. 112°/12 mm. 1-*Methyl*-3-α-*bromoethylbenzene*, $C_6H_4Me·CHBrMe$, a colourless liquid, b. p. 101°/12 mm. (βγ-*Di*-m-*tolylbutane*, $C_6H_4Me·CHMe·CHMe·C_6H_4Me$, crystallises in slender, lustrous needles, m. p. 97°.) 1-Methyl-3-ethylbenzene (from *m*-methylacetophenone by Clemmensen's method), b. p. 159·7—160·5°, $d_4^{19·9}$ 0·8669, $d_4^{20}$ 0·867, $n_\alpha^{19·9}$ 1·49575, $n_D^{19·9}$ 1·49966, $n_\beta^{19·9}$ 1·51102, $n_\gamma^{19·9}$ 1·52056; (from 1-methyl-3-α-bromoethylbenzene), b. p. 159°, $d_4^{19·8}$ 0·8622, $d_4^{20}$ 0·862, $n_\alpha^{19·8}$ 1·49279, $n_D^{19·8}$ 1·49650, $n_\beta^{19·8}$ 1·50767, $n_\gamma^{19·8}$ 1·51678. *p*-Tolylmethylcarbinol, b. p. 108/12 mm., is oxidised to *p*-methylacetophenone, b. p. 105—106°/13 mm., $d_4^{18·4}$ 1·0045, $d_4^{20}$ 1·003, $n_\alpha^{18·4}$ 1·52880, $n_D^{18·4}$ 1·53391, $n_\beta^{18·4}$ 1·54835, $n_\gamma^{18·4}$ 1·56127, $n_D^{20}$ 1·5332, which is identical with a product prepared by the Friedel-Crafts reaction. 1-*Methyl*-4-α-*bromoethylbenzene*, a colourless liquid, b. p. 105—106°/12 mm. 1-Methyl-4-ethylbenzene (from *p*-methylacetophenone by Clemmensen's method), b. p. 160·5°, $n_D^{21·5}$ 1·49424, $n_D^{20}$ 1·49490; from the Friedel-Crafts ketone), b. p. 161°, $d_4^{16·8}$ 0·8650, whence $d_4^{15·9}$ 0·8657, $d_4^{20}$ 0·862, $n_\alpha^{15·9}$ 1·49372, $n_D^{15·9}$ 1·49775, $n_\beta^{15·9}$ 1·50889, $n_\gamma^{15·9}$ 1·51833; (from 1-methyl-4-α-bromoethylbenzene), b. p. 160°, $n_D^{24·4}$ 1·49287, $n_D^{20}$ 1·49481. *m*-Tolylethylcarbinol, b. p. 114°/12—13 mm. 1-Methyl-3-α-*bromopropylbenzene*, a colourless liquid, b. p. 114°/14 mm. 1-Methyl-3-propylbenzene (from the bromide), b. p. 180°, $d_4^{17·6}$ 0·8646, $d_4^{20}$ 0·863, $n_\alpha^{17·6}$ 1·48968, $n_D^{17·6}$ 1·49340, $n_\beta^{17·6}$ 1·5038; (from *m*-bromotoluene, propyl bromide, and sodium), b. p. 177—178·5°, $d_4^{20}$ 0·8601, $n_\alpha^{20}$ 1·48978, $n_D^{20}$ 1·49321, $n_\beta^{20}$ 1·50392. p-*Tolylethylcarbinol* is a colourless liquid, b. p. 114°/12—13 mm 1-Methyl-4-α-*bromopropylbenzene*, a colourless liquid, b. p. 108°/13 mm. *p*-Propionyltoluene, b. p. 114°/14 mm. 1-Methyl-4-propylbenzene (from the corresponding bromide), b. p. 182°, $d_4^{18·8}$ 0·8620, $d_4^{20}$ 0·861, $n_\alpha^{18·8}$ 1·49278, $n_D^{18·8}$ 1·49655, $n_\beta^{18·8}$ 1·50765, $n_\gamma^{18·8}$ 1·51687; (from *p*-propionyltoluene, according to Clemmensen) b. p. 183°, $d_4^{20}$ 0·860, $d_4^{18·8}$ 0·8617, $n_\alpha^{18·8}$ 1·49269, $n_D^{18·8}$ 1·49641 $n_\beta^{18·8}$ 1·50752; (by reduction of the ketone prepared by the Friedel-Crafts method), b. p. 182·5°, $n_D^{20}$ 1·49542; (from *p*-bromotoluene propyl bromide, and sodium), b. p. 181—181·5°, $d_4^{23·7}$ 0·8554 $d_4^{20}$ 0·858, $n_\alpha^{23·7}$ 1·48706, $n_D^{23·7}$ 1·49065, $n_\beta^{23·7}$ 1·50119. 1-Methyl-*cyclo*hexan-4-ol, b. p. 172—173°, $d_4^{16·3}$ 0·9192, $d_4^{20}$ 0·916, $n_\alpha^{16·3}$ 1·45742 $n_D^{16·3}$ 1·45959, $n_\beta^{16·3}$ 1·46558, $n_\gamma^{16·3}$ 1·47025, $n_D^{20}$ 1·4579. 1-Methyl*cyclo*hexan-4-one, b. p. 169·2°, $d_4^{19·9}$ 0·91685, $d_4^{20}$ 0·917, $n_\alpha^{19·9}$ 1·44285 $n_D^{19·9}$ 1·44509, $n_\beta^{19·9}$ 1·45110, $n_\gamma^{19·9}$ 1·45595, $n_D^{20}$ 1·4450. H. W.

**Occurrence of Spark Lines (Enhanced Lines) in the Arc th Lead and Tin.** G. A. HEMSALECH and A. DE GRAMONT (*Phil. Mag.*, 1922, **43**, [vi], 287—306).—A convenient method is

described for obtaining the arc spectra of volatile metals. This consists in placing a piece of the metal on a sheet of copper (5 cm. × 10 cm. × 1 mm.) and connecting to the positive pole. The negative pole is a pointed carbon rod; the arc is struck by lowering the point until it touches the metal and then withdrawing it a little. The metal melts and forms a globule and the arc between it and the carbon point burns steadily. The heat generated is dissipated by the copper plate. Experiments are described which seem to indicate that spark lines are brought out in the arc when the degree of ionisation is reduced, as, for example, by blowing air through the arc. The effect of liquid media on the character of the arc spectrum of the metal has been studied by placing a drop of the liquid between the poles before striking the arc. The spark lines, or so-called high temperature lines, disappear from the arc when the cathode is formed by white-hot carbon, but they are brought out prominently when the electrodes are cooled down to about $-190°$ by immersion in liquid air. A detailed account is given of the observations on the relative behaviour of various types of lead and tin lines in the arc under various conditions of discharge. It is definitely shown that the presence of hydrogen is not essential for the excitation of spark lines. Spark lines attain a high degree of development only in a medium which offers a comparatively high resistance to the flow of electricity. When hydrogen is present in the medium, either free or in combination, its spectrum resembles that which is only observed with high tension condenser discharges; namely, its lines are symmetrically broadened as though under the influence of a strong electric field (Stark effect). J. F. S.

**Röntgen Absorption Spectrum of Chlorine.** AXEL E. LINDH (*Z. Physik*, 1921, **6**, 303—310).—The Röntgen absorption spectrum of chlorine has been examined, using free chlorine and the compounds lithium, sodium, potassium, and thorium chlorides, potassium chlorate, potassium perchlorate, ammonium stannichloride and dichlorotetra-aquochromium chloride, $(Cr[H_2O]_4Cl_2)Cl$. It is shown that with univalent chlorine in all cases the absorption edge has the same wave-length, within the limits of the experimental error. In the case of qninque- and septa-valent chlorine, a displacement of the absorption edge toward shorter wave-lengths is observed which is greatest in the case of septavalent chlorine. A metallic Röntgen tube and new apparatus for photometric measurements both designed for measurements of the above-named type are described. J. F. S.

**Series Regularities in the Resonance Spectrum of Iodine.** R. MECKE (*Z. Physik*, 1921, **7**, 73—85).—A theoretical paper in which, on the basis of Wood's measurements of the resonance spectrum of iodine (A., 1911, ii, 82, 950; 1912, ii, 325, 1018; 1913, ii, 994; 1914, ii, 233; "Researches in Physical Optics," II, 1919), which is shown to consist of a series of doublets of the band type and is expressed by the series formula $\nu = A + Bm + Cm^2 + Dm^3$, the author has examined the series regularities of this spectrum.

It is shown that the first constant is given invariably by the exciting line, whilst the two final coefficients, $C$ and $D$, maintain their values at all exciting lines. On the other hand, the second factor varies, but this may be represented in the form $B=b_0-b_1n$, in which $n$ is a whole number, so that a number of partial series can be differentiated. In the case of the most accurately investigated resonance spectrum, that of the green mercury line, eight such series of doublets can be characterised, which can also, according to the position of the components of the doublets, be divided into two groups. In one group, $b_1$ has the value 0·655, and, in the other, 0·75, and $n$ can have the values 0, 1, 2, and 3. For $n=0$ an apparent triplet is indicated. Further regularities are probable in the series, but they cannot be definitely characterised. It appears that the value of $m$ represents an azimuth quantum number. In consequence of the very small moment of inertia, however, the rotation cannot be ascribed to the molecule itself; it is therefore assumed that the moment of inertia is due to a rotating electron ring. On this assumption, the series formula can be developed, and resolved into the two energy terms. Further, it is shown that resonance spectra, in the same way as line spectra, are brought into existence by electron springs.

J. F. S.

**Divergence from Stokes's Law during the Excitation of the Fluorescence of Iodine Vapour.** PETER PRINGSHEIM (*Z. Physik*, 1921, 7, 206—216).—The resonance spectrum of iodine vapour has been examined. It is shown that on heating the vapour from the ordinary temperature to 320°, the intensity of the anti-Stokes members increases many times, and at the same time also that of the members of positive order number some become stronger whilst the majority become less bright. It is thought probable that these oppositely behaving resonance lines belong to series which originate from some of the seven iodine absorption lines covered by the mercury line. J. F. S.

**Difference between the Absorption Spectrum and the Complete Fluorescence Spectrum of Iodine Vapour indicated by Lenz's Theory.** PETER PRINGSHEIM (*Z. Physik*, 1921, 8, 126—131).—Theoretically, it is to be expected that the members of higher order number in the resonance spectrum of cold iodine vapour will not be markedly absorbed; this conclusion is fully confirmed by experiment. Correspondingly, the fluorescence spectrum of iodine vapour excited by white light is not a simple reversal of the absorption spectrum, but is considerably richer in lines, and so the colour change of the fluorescence of iodine vapour of high density is explained by a partial reabsorption of the fluorescence light. In iodine vapour at higher temperatures, resonance lines of higher order number are also strongly absorbed. The colour change in the emission spectrum of iodine vapour of constant density, occasioned by fluoresence or electric discharge at higher temperatures is considered, and it is shown that the cause cannot, at present, be indicated theoretically. J. F. S.

**Ultra-red Reflection Power of Silica.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, 7, 313—315).—The reflection spectra of various varieties of silica has been measured; the varieties include quartz, chrysoprase, hornstein, chalcedony, opal, and quartz-glass. It is shown that all varieties except the last two exhibit an identical quantitative reflection power. The reflection maximum at about 9$\mu$ exhibits about 90% of the metallic reflection. In the case of opal and quartz-glass, the reflection maximum lies in the same position as in the other varieties, but the reflection power has fallen to 40—50%. This result is attributed to a distortion of the space lattice in the amorphous varieties of silica. It is remarkable that the water maximum, which lies at 3·2$\mu$, is not observed in the case of opal and it is suggested that this is to be attributed to the probable fact that the water is not arranged in the space lattice in opal. J. F. S.

**The *L* Doublet of Neon.** WALTER GROTRIAN (*Z. Physik*, 1921, 8, 116—125).—From a consideration of the recent work on the systematics of examination of Röntgen spectra, the view is put forward that only one permanent condition of unexcited atoms exists, and that the different absorption band edges are to be explained, not by different initial conditions, but by different final conditions. From this, the conclusion is drawn that of the inactive gases helium has one ionisation-potential, neon three, argon five, and krypton seven. In the case of neon, it is shown that the doublet difference, $L_2—L_1$, is identical with the constant $A$ found by Paschen for the neon spectrum, $A=782$ cm$^{-1}$. The absolute value of the ionisation potential of neon has as yet not been determined with certainty. J. F. S.

**Characteristic Ultra-red Frequencies of Selenates and Chromates.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, 7, 297—308).—The reflection spectra of potassium, manganese, nickel, copper, zinc, and cadmium selenates, an isomorphous mixture of lithium and sodium selenate, magnesium ammonium selenate, manganese ammonium selenate, nickel ammonium selenate, cobalt ammonium selenate, nickel potassium selenate, and zinc potassium selenate have been determined in the region of the ultra-red, using ordinary light. It is shown that all selenates exhibit in the region 11$\mu$ a definite maximum of the reflection power, which is to be attributed to the vibrations of the selenate radicle. This maximum is analogous to the maximum at 9$\mu$ exhibited by the sulphates (cf. A., 1916, ii, 505, 506; 1918, ii, 282, 315). In those cases where the selenates contain water of crystallisation, the water bands previously recorded (*loc. cit.*) are also observed. The crystals have also been examined in polarised light, and it is shown that the reflection maximum at about 11$\mu$ can be resolved into two groups of characteristic vibrations in the case of uni-axial crystals and into three in the case of bi-axial crystals. Similar measurements were made with potassium chromate, sodium potassium chromate, magnesium ammonium chromate, and potassium dichromate. In the first three cases

using ordinary light, a single well-developed maximum is found, which lies respectively at 11·16μ, 11·2μ, and at complex maximum 11·3μ and 11·42μ. In the case of potassium dichromate, three maxima are observed, the first two of which are complex and lie at 10·44μ and 11·1μ, 12·14μ and 13·22μ, and 18·12μ. Magnesium ammonium chromate has been examined in polarised light and exhibits a maximum at 11μ which falls into three groups: 11·46μ parallel to the *a* axis, 11·28μ parallel to the *b* axis, and 10·36μ parallel to the *c* axis. J. F. S.

**Characteristic Ultra-red Frequencies of Chlorates, Bromates, and Iodates.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, **7**, 309—312).—The reflection spectra of sodium, potassium, silver, and barium chlorates, sodium, silver, cadmium, and barium bromates and potassium iodate have been measured. It is shown that in all cases but that of sodium bromate, where a single maximum is observed, two reflection maxima are exhibited. The maxima have the following wave-lengths: sodium chlorate, 10·04μ, 16·04μ; potassium chlorate, 10·12μ, 16·22μ; silver chlorate, 10·76μ, 16·38μ; barium chlorate, 10·24μ, 19·6μ; sodium bromate, 12·24μ; silver bromate, 12·62μ, 13·10μ; cadmium bromate, 12·32μ, 13·20μ; barium bromate, 12·3μ, 12·64μ, and potassium iodide, 12·48μ, 13·16μ. The values are discussed in connexion with those found for other acid radicles (cf. preceding abstract). J. F. S.

**Röntgen Spectra.** ELIS HJALMAR (*Z. Physik*, 1921, **7**, 341—350).—Röntgen spectra of the elements copper to tantalum have been measured. It is shown to be probable that the $\beta_1$ lines of the *K* series of the lighter elements are not simple. This has been established in the case of sulphur. The new line is regarded by the author as the continuation of the $\beta_2$ line of the next higher element, and the theoretical significance of this is discussed. The valency of sulphur appears to have no action on the emission spectra, but the experimental difficulties experienced in the work make it advisable to leave this question open. Exact measurements of a number of lines of the *K*-series are recorded, and the earlier measurements of lines of the *L* series are controlled. Two long tables of wave-lengths measured in the present work are included in the paper. J. F. S.

**Systematics of Röntgen Spectra.** D. COSTER (*Z. Physik*, 1921, **6**, 185—203).—The author has measured the Röntgen spectra of the elements tantalum, tungsten, osmium, iridium, platinum, gold, thallium, lead, bismuth, thorium, and uranium, using the method adopted by Hadding (*ibid.*, 1920, **3**, 369). The object of the work was to obtain measurements of the very weak lines and from these to examine various relationships and regularities obtaining among *X*-ray spectra. Tables of the lines measured are given in the paper and also of the *L* doublets; a table of the constant wave-length differences $\beta_2-\beta_5$, $\gamma_1-\gamma_6$, $\gamma_2-\gamma_3$, $\beta_4-\beta_5$, $\beta_2-\beta_8$, and $\beta_2-\beta_7$ is drawn up. The relationship $(L_3-L_1)-M\gamma=L\beta_3-L\beta_2$, put forward

by Smekal (A., 1921, ii, 615), is evaluated and found to be only in moderate agreement with the experimental data; the divergences between the two sets of values are attributed to errors in the $(L_3-L_1)$ values. J. F. S.

**Systematics of Röntgen Spectra.** ADOLF SMEKAL (*Z. Physik*, 1921, 7, 410—412).—A reply to Coster (preceding abstract). The author points out that Coster's criticism is based on a misunderstanding of his method of treatment. J. F. S.

**Fluorescence of Cadmium Vapour.** J. STEPH. VAN DER LINGEN (*Z. Physik*, 1921, 6, 403—404).—Light from cadmium sparks was allowed to pass through an evacuated quartz globe at 280° containing a scrap of cadmium. It is found that an absorption line 2288 Å.U. appears at this temperature, and with changing vapour density a band symmetrical with this line appears. When the band extends to 2307 Å.U. a second absorption line, 3260 Å.U. is observed. To ascertain whether the emitted light is due to resonance or fluorescence, the cadium light around 2288 Å.U. was isolated and passed through the globe. It was found that at a density corresponding with that at which the line 2288 Å.U. is emitted, the vapour shows an ultra-violet fluorescence band which is sharply terminated at 2288 Å.U. and fades at 2314 Å.U. At higher densities the head disappears at 2288 Å.U., and the band is then terminated at 2313 Å.U. and extends to 3005 Å.U., where it also ends sharply. Between 2745 and 3005 Å.U. the band contains sixteen lines which are closer together the smaller the wave-length. J. F. S.

**Dependence of the Intensity of the Fluorescence of Dyes on the Wave-length of the Exciting Light.** S. I. VAVILOV (*Phil. Mag.*, 1922, [vi], 43, 307—320).—It has been shown by Nichols and Merritt (*Physical Rev.*, 1910, 31, 376, 381) that the specific fluorescence of resorufin and eosin increases toward long wave-lengths. The present paper describes experiments with fluorescein, eosin-S extra, and rhodamine-B extra, designed to test how far this result is general. It is shown that within the limits of the errors of observation the specific fluorescence of the dyes mentioned is independent of the wave-lengths of their absorption bands. This result is equivalent to the conclusion that the absorption curves of the dyes are physically simple ones. Einstein's theory is not confirmed, but the deviations required by this theory are so small that they are only a little greater than the experimental errors, and consequently no very definite statement can be made. The intensity of fluorescence radiated by a definite molecular resonator depends only on the valne of the absorbed energy and on the mechanism of the resonator. In the case of excitation by white light, the intensity of fluorescence $F$ can therefore be expressed by the equation $F=K\int_{\lambda_1}^{\lambda_2} I_\lambda \, . \, xc.e^{-xcd} \, . \, d\lambda$, where $I_\lambda$ is the energy of the exciting source in the wave-length interval $\lambda \ldots \lambda+d\lambda$, $xc$ the coefficient of absorption of the solution over the same wave-length interval, $C$ the

concentration, and $K$ the specific fluorescence. The result of Nichol and Merritt (*loc. cit.*) probably only shows the physical complexity of the bands of the dyes examined by them. J. F. S.

**Ionisation brought about by Quinine Salts.** GERHARD C SCHMIDT (*Z. Physik*, 1921, **8**, 160—164).—It is shown that quinine nitrate as well as quinine sulphate (Le Bon, *Compt. rend.*, 1900, **130** 891) emits light on warming and makes the surrounding air a conductor; other salts of quinine have no such action. All quinine salts when heated to just above the melting point change into a modification which gives intensely green fluorescent solutions instead of the usual violet fluorescent solutions. Quinine hydrogen sulphate in aqueous or chloroform solution gives a violet fluorescence but when heated at 50° for an hour the fluorescence is light blue when heated to the melting point this changes to an intense green which is maintained at very high dilutions. In the case of quinine valerate, the green colour changes back to violet on dilution when in water solution; in chloroform solution the heated salt gives a green fluorescence, but a violet fluorescence in benzene. The absorption spectrum of the green fluorescing solution is different from that of the violet fluorescing solution. The following hypothesis is advanced to explain the luminescence of the nitrate and sulphate when warmed, and its absence in other salts. On heating, these two salts pass into a new modification, which on stronger heating passes into the green, fluorescing variety; the change into the intermediate modification is accompanied by the emission of electrons or ions In the case of the other salts, there is no intermediate compound formed, but a direct change into the green, fluorescing variety without emission of ions or electrons. J. F. S.

**Action of Light on Silver Chloride, Bromide, and Iodide** PETER PAUL KOCH and FRITZ SCHRADER (*Z. Physik*, 1921, **6**, 127—131).—The results of experiments, made to ascertain the loss of weight of particles of silver chloride, silver bromide, and silver iodide on illumination, previously published (A., 1921, ii, 289) and a large number of other experiments made by the same method are collected and considered. The experiments were made with the suspended particles in air, dried air, dry nitrogen, moist nitrogen moist argon, and dry argon, and a number of improvements were made in the technique of the method. The results show that silver chloride illuminated by intensities up to 3,000,000, silver bromide up to 12,000,000, and silver iodide up to 5,600,000 candle metre seconds (the light coming from the positive crater of an arc through 80 cm. of 1% copper sulphate solution) do not undergo a change in weight greater than 1—2%. The larger changes previously recorded are attributed to disturbances in the earlier experiments among which the secondary reaction of silver bromide with the surrounding gas is mentioned. The rate of colouring of the silver haloids by light has also been determined; it is shown that silver bromide, after an illumination of 5 seconds by a light of intensity 3200 candle metre seconds, shows a definite coloration, silver chloride shows a coloration in three minutes when illuminated by

940 candle metre seconds, and silver iodide after ten minutes' illumination by the same light shows only a weak greyish-black coloration. In all cases the coloration increases with the duration of the illumination. J. F. S.

**Luminous Path of α-Rays in Crystals.** H. GEIGER and A. WERNER (*Z. Physik*, 1921, **8**, 191—192).—An experiment is described which answers the question, "Is the number of metallic centres, which are excited by an α-particle on its entry into a crystal, sufficiently great in every case to bring about a visible scintillation?" A thin, highly polished section of artificial willemite was arranged in the field of a microscope so that the α-rays from a polonium preparation should strike it at a small angle. At a magnification of 400, point scintillations were not seen, but luminous lines of 0·02 mm. length. These represent the path of the α-particle in the crystal, and show that the number of centres is extremely large, and in the case of perfect crystals sufficient to ensure a scintillation for every α-particle hitting the crystal. J. F. S.

**The Meitner Nuclear Model of the Radio-elements as the Basis of a Relationship between the Range and Total Number of Nuclear Particles of the α-Radiators.** MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 327—331).—A theoretical paper in which, on the basis of the Meitner nuclear model, a relationship between the range and the total number of nuclear particles of the α-radiators is deduced. The range of most of the α-radiators of the uranium, thorium, and actinium families is calculated by means of this new relationship and found to be in good agreement. The divergence of the two sets of values lies between $\pm 0·8\%$ and $\pm 1·8\%$. Applying this relationship to the hypothetical elements uranium III and uranium IV, it is found that the former is practically inactive whilst the latter has a much shorter life than uranium I. This is further evidence against the existence of these hypothetical isotopes (cf. this vol., ii, 85). J. F. S.

**Beta Rays and Atomic Number.** J. L. GLASSON (*Phil. Mag.*, 1922, [vi], **43**, 393—396).—A theoretical paper in which the relationships between the atomic absorption, α, and the atomic scattering, β, of β-rays respectively and the atomic number are considered. The values of α, β, the atomic absorption $a=\alpha A/D$, the atomic scattering $b=\beta A/D$, the atomic weight $A$, the density $D$, and the atomic number $N$ are tabulated for a number of elements from magnesium to bismuth. It is shown from the table that the values of $a$ are approximately constant for elements of the same period of the periodic system; the elements examined fall into four groups which have values for $a$ in the ratio 1 : 2 : 3 : 4. These groups are magnesium and aluminium, $a=89$; iron, cobalt, nickel, copper, and zinc, $a=172$—$196$; palladium, silver, and tin, $a=260$—$268$; and platinum, gold, lead, and bismuth, $a=348$—$372$. It therefore seems likely that the value of $a$ is a periodic function of the atomic number. The value of $b$ increases with the atomic number of the element and on plotting $\log b$ against $\log N$ a curve is obtained

which is represented by $\log b = 2{\cdot}09 \log N - 0{\cdot}44$ and therefore $b = 0{\cdot}36 \times N^{2{\cdot}09}$. J. F. S.

**Scattering of Röntgen Rays by the Atoms of a Crystal.** W. L. Bragg, R. W. James, and C. H. Bosanquet (*Z. Physik*, 1921, **8**, 77—84).—A theoretical paper in which the experimental results previously published (A., 1912, ii, 477) on the scattering of Röntgen rays by the sodium and chlorine atoms of rock-salt crystals have been used in connexion with the arrangement of the electrons inside the atom. In the case of the sodium atom, the expected amplitude curve has been calculated for the case that of the eight exterior electrons four vibrate in di-quantic circular orbits and four in di-quantic elliptical orbits, and it is shown that such a model has a very satisfactory agreement with the experimental facts. J. F. S.

**Characteristic *X*-Rays from Boron and Carbon.** A. Ll Hughes (*Phil. Mag.*, 1922, [vi], **43**, 145—161).—The photoelectri effect of the radiation from carbon and boron bombarded b electrons has been measured as a function of the energy of th electrons. Two slight but definite breaks in the curves for bot carbon and boron were obtained. These are considered to cor respond with the *K*- and *L*-absorption wave-lengths. The break occur at 215 volts ($\lambda = 57{\cdot}5$) and 34·5 volts ($\lambda = 358$) for carbo and 148 volts ($\lambda = 83{\cdot}5$) and 24·5 volts ($\lambda = 505$) for boron. Th *L* point for carbon is in good agreement with the measured value recently obtained by Millikan (*Astrophys. J.*, 1920, **52**, 47) for th *L* emission lines of carbon vapour. The *K* points for carbon an boron are approximately where they would be expected on extra polating the known values of the $K_a$ critical absorption wave-length for elements heavier than magnesium. J. F. S.

**Absorption of the *K X*-Rays of Silver in Gases and Gaseou Mixtures.** P. W. Burbidge (*Phil. Mag.*, 1922, [vi], **43**, 381—389).—The total absorption coefficient of silver *K* radiation ha been measured in air, carbon dioxide, sulphur dioxide, and methy iodide vapour. Using the same silver *K* radiation, it has bee shown with mixtures of sulphur dioxide and air, carbon dioxid and air, sulphur dioxide and carbon dioxide, and methyl iodide an air that the absorption in gases is atomic (as in the case of solid and liquids) and therefore additive in mixtures and compounds. J. F. S.

**Experimental Decision of the Question of the Radioactivit of all Elements. II.** G. Hoffmann (*Z. Physik*, 1921, **7**, 254—259; cf. A., 1920, ii, 575).—Making use of the very sensitive metho of measuring α-ray activity previously described (*loc. cit.*), th author has extended his measurements to platinum. The measurin instrument itself shows an α-ray activity represented by 0·3—0· α-particle per hour. Using a cleaned platinum dish of 39 sq. cm surface, an activity of 14·6 per hour for the whole dish is recorded or 0·39 per sq. cm. The measurements were made over a perio of about fifty hours. The results are analysed for α-rays whic

may come from known α-radiators of all ranges uniformly distributed through the mass of the platinum and for α-radiators situated on the surface of the platinum, and the analysis indicates a definite α-ray activity of platinum. J. F. S.

**Protactinium Content of Pitchblende Residues and the Branching Relationship of the Actinium Series.** OTTO HAHN and LISE MEITNER (*Z. Physik*, 1921, **8**, 202—204).—A criticism of the value put forward by St. Meyer (*Mitt. Inst. Rad. Forsch.*, 1920, 127) for the branching relationship of the actinium series. The value, 4·2%, is about 25% higher than that found by the present authors, 3±0·3%. It is shown to be probable that Meyer's preparation contained 1—2% of ionium, which would explain the difference in the two figures. J. F. S.

**Existence of Isotopes of Uranium and the Meitner Nuclear Model.** MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 321—326).—The author discusses the position of uranium-$Z_2$ in the disintegration series from the point of view of Meitner's *nuclear model. The position given by Hahn (A., 1921, ii, 498)* in the series $U_{III} \xrightarrow{\alpha} UZ_1 \xrightarrow{\beta} UZ_2 \xrightarrow{\beta} U_{IV}$ is criticised, and it is shown, for several reasons, that only two elements of the uranium type, uranium I and uranium II, can possibly exist. The elements uranium II and uranium III are shown to be identical and the disintegration series:

$$U_I \begin{cases} \xrightarrow{\alpha} UX_1 \xrightarrow{\beta} UX_2 \xrightarrow{\beta} \\ \xrightarrow{\alpha} UZ_1 \xrightarrow{\beta} UZ_2 \xrightarrow{\beta} \end{cases} U_{II} \begin{cases} \rightarrow Io \\ \rightarrow UY \end{cases}$$

is put forward to represent the disintegration of uranium. A method for the detection of isotopes of the fourth order (this vol., ii, 107) is described. It consists in determining the number of particles emitted by the disintegrating substance; should this number be in keeping with the disintegration constant, then the substance does not consist of isotopes of the fourth order, but of a single element. J. F. S.

**A New Radioactive Substance.** A. PICCARD and E. STAHEL (*Physikal. Z.*, 1922, **23**, 1).—A quantity of uranium-$X$, separated from uranyl nitrate by the ether–water method, has been repeatedly measured with respect to its β-radiation for a prolonged period. It is shown that in addition to the hard β-radiation of uranium-$X$, there is a soft radiation which with increasing age of the preparation decreases more and more slowly; this indicates the presence of a substance of longer life than uranium-$X$. This substance has been provisionally named uranium-$V$. It has an approximate half life of forty-eight days, or abont twice as long as uranium-$X_1$. The β-radiation due to this element is half absorbed by an aluminium sheet 0·003 mm. thick, that is, the absorption coefficient is 2300 $cm.^{-1}$ Al. It is shown that this substance may be a member of the actinium series, but it has not been decided whether it or uranium-$Y$ is the first thorium isotope in the disintegration series put forward by one of the authors. J. F. S.

**Some Oxidising Properties of Thorium-*X*.** PIERRE LEMAY and LÉON JALOUSTRE (*Compt. rend.*, 1922, **174**, 171—172).—Thorium-*X* exerts a very marked catalytic action in the oxidation of adrenaline and morphine, the oxidation being much more rapid than in the presence of manganese salts. Oxidation could not, however, be proved in the case of the primary alcohols of the fatty series. W. G.

**Ionisation Tension of the Halogen Hydrides.** PAUL KNIPPING (*Z. Physik*, 1921, **7**, 328—340).—The ionisation tension of hydrogen cyanide, chloride, bromide and iodide has been determined by the method previously described by Franck and Knipping for helium (A., 1920, ii, 72). The following values are recorded: hydrogen cyanide, 15·5 volts, 357 Cal.; hydrogen chloride, 14·4 volts, 331 Cal.; hydrogen bromide, 13·8 volts, 317 Cal.; and hydrogen iodide, 13·4 volts, 308 Cal. The electron affinity, in Cal. and volts, the limiting wave-length, and frequency have been calculated for chlorine, bromine, and iodine, and the values compared with those of other investigators. The following values are recorded: chlorine, 98 Cal., 4·26 volts, $\lambda=2890$, $\nu=34600$; bromine, 68 Cal., 2·96 volts, $\lambda=4150$, $\nu=24100$, and iodine, 61 Cal., 2·65 volts, $\lambda=4600$, $\nu=21500$. J. F. S.

**Ionisation and Excitation Tension of Nitrogen.** ERICH BRANDT (*Z. Physik*, 1921, **8**, 32—44).—The ionisation tension of nitrogen has been found to be $17·75\pm0·1$ volt with reference to the resonance tension of helium, 20·5 volts. Higher ionisation stages have been found at $25·41\pm0·1$ volt and $30·72\pm0·2$ volt, both with reference to the value 17·75 volts. The limits of light excitation of the nitrogen molecule by electron collisions have been investigated, and an analogy between the light-electric curve and that of band emission is pointed out. J. F. S.

**Electrical Conductivity of Zinc Sulphate Solutions in the Presence of Sulphuric Acid.** HERMAN V. TARTAR and HARMON E. KEYES (*J. Ind. Eng. Chem.*, 1921, **13**, 1127—1129).—The conductivity of zinc sulphate solutions increases with the sulphuric acid concentration, but the conductivity of sulphuric acid is decreased by the addition of zinc sulphate; when magnesium sulphate is added to a strongly acid zinc sulphate solution, an additional decrease in conductivity occurs. The addition of small quantities of gelatin does not affect the conductivity. The temperature coefficients of conductivity vary, and are a function of the acid and zinc concentration. During the electrolysis of zinc sulphate solutions there is an increase in the volume of the solution, the increase amounting to 1·5% for each 100 grams of zinc deposited. W. P. S.

**Anomalous Dissociation in Aqueous Solutions.** A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, **99**, 338—360).—By anomalous dissociation is understood the phenomenon which occasions a decrease in the molecular or equivalent conductivity

with increasing dilution, that is, the degree of dissociation, as expressed by $\alpha=\lambda/\lambda_{\infty}$, decreases with increasing dilution. With the object of finding a connexion between the viscosity and the electrical conductivity of solutions of salts in water, the author has determined the density, viscosity, and electrical conductivity of aqueous solutions of cæsium chloride, cadmium chloride, cadmium bromide, cadmium iodide, zinc bromide, zinc iodide, and sodium iodide at 0°, 25°, and 50°. It is shown that in the case of cæsium chloride the viscosity and the conductivity are very closely connected. A comparison of the corrected molecular conductivity curves and the relative viscosity curves at 25° and 50° for the halogen salts of cadmium with one another and with those of other salts shows that the form of the relative viscosity curve has a strong influence on the form of the $\lambda\eta_a$ curve. In those cases with a high value for $\eta_a$, the introduction of the usual viscosity correction of the $\lambda\eta_a$ curves can lead to an anomalous form of the curve because of over-correction. This anomaly is general in the case of highly concentrated aqueous solutions. The over-correction is explained as follows : In introducing the correction, it is assumed that the ionic mobility is inversely proportional to the viscosity of the medium. This assumption, however, does not hold because a reduction of the ionic diameter is brought about by increasing concentration, due largely to a dehydration of the ions. With increasing temperature, the anomaly extends over a considerable portion of the $\lambda\eta_a - V$ curve. This is in opposition to the view that the anomaly is due solely to the over-correction on account of a reduction of the ionic diameter. If the over-correction is due alone to the inapplicability of Stokes's law to all concentrations, then it is to be expected that the minimum, displaced on warming, should correspond with higher viscosity values; but since this is only observed in the case of cæsium chloride, it follows that this cause of over-correction does not explain the anomaly in all cases. It is held that the anomalous form of the conductivity curve is not to be explained by the over-correction alone, but is due to several causes. It is suggested that the causes which bring about the "true anomalous dissociation" in non-aqueous solutions are operative in aqueous solutions also. This suggestion would explain the displacement of the minimum with increasing temperature, since with increasing temperature water in respect of its dielectric constant approaches in behaviour the other solvents. It is also shown that in concentrated aqueous solutions, in addition to the over-correction of the conductivity values, there is also a typical anomalous progression of the molecular and equivalent conductivity, which in all probability has its origin in the same causes as in non-aqueous solutions. J. F. S.

**Electrolytic Dissociation of Salts in Concentrated Solutions, and in the Fused and Solid States.** A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, **99**, 417—433; cf. preceding abstract).—The conductivities, viscosities, and densities of aqueous solutions of cæsium chloride, silver nitrate, ammonium nitrate, thallium

nitrate, and thallium silver nitrate were determined at high concentrations. In the case of thallium ammonium nitrate the results were extended to the fused salt. The molecular conductivities were extrapolated to the pure salts. After the application of the viscosity correction, all the molecular conductivity curves assumed an abnormal form, and on extrapolation to pure salt gave high values of $\mu\eta_a$, where $\mu$ is the molecular conductivity and $\eta_a$ the relative viscosity. The values of $\mu\eta_a/\mu_\infty = \alpha$ were therefore abnormally high. The true values of $\alpha$ for the salts probably lie between the values calculated from the corrected and the uncorrected $(\mu/\mu_\infty)$ conductivities, and nearer the former. The course of the dissociation in very concentrated solutions is thus abnormal. The extrapolation was confirmed by the form of the curve for thallium silver nitrate, which continued smoothly up to the fused salt. J. R. P.

**Reversal of the Molecular Conductivity Curve and Abnormal Dissociation.** A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, 99, 434—453; cf. preceding abstract).—Abnormal dissociation occurs when the degree of dissociation (or the molecular conductivity) decreases with increasing dilution. It is most commonly observed with non-aqueous solutions, and is most marked when the dielectric constant of the solvent is small. The various hypotheses which have been advanced to account for the phenomenon are reviewed. In the ordinary method of representation of conductivities, the dilution $V$ is taken as the variable volume of solution in which a constant weight of one gram equivalent of solute is dissolved. The author considers the results obtained when a constant weight of one gram equivalent of solvent is taken and the volume $V_1$ of solution containing it is taken as the dilution. If $k$ is the specific conductivity, the product $kV_1 = \mu_1$ is the newly-defined molecular conductivity. The curves representing the values of $\mu_1$ and $V_1$ are called "reversed conductivity curves." When only one constituent of the solution is capable of ionisation and the other is a strong ioniser (for example, acetic acid in water), the original molecular conductivity curve is normal but the reversed curve is abnormal, exhibiting a maximum but not a minimum, after correction for viscosity. When the ionising constituent is also a strong ioniser (for example, silver nitrate in aniline or water), the original curve is abnormal, without a maximum, or apparently abnormal (without correction). The reversed curve is normal (water in silver nitrate and thallium silver nitrate), or, in consequence of the uncorrected increase in viscosity is apparently abnormal (aniline in silver nitrate). When neither constituent is ionisable, but when its polymeride or solvate is ionisable, then in both cases abnormal curves result, in the latter case with a maximum, the position of which indicates approximately the maximum content of solvate in the solution. To the right and left of the maximum the conductivity decreases in consequence of the diminution of solvation due to insufficient quantity of solvent and to depolymerisation respectively. Examples of such curves are

rnished by acetic acid and aniline and by acetic acid and pyridine. definition of abnormal dissociation is given. J. R. P.

**Effective Potential Difference of Electro-osmosis and llied Phenomena.** H. FREUNDLICH (*Trans. Faraday Soc.*, )21, **16**, Appendix, 146—149).—A theoretical paper in which the ıthor discusses the nature of the potential difference at work electro-osmosis, cataphoresis, and allied phenomena. A great ;al of experimental work is reviewed, and it is shown that .e Nernst potential difference, $\epsilon$, is in no sense identical with ıe electrokinetic potential difference, $\zeta$; the Nernst potential presents the total difference between the interior of the first ıase and that of the second phase, the electrokinetic potential presents that portion of the difference which falls within the splaceable liquid layers. J. F. S.

**Selenium [Cells].** WILHELM SPÄTH (*Z. Physik*, 1921, **8**, ;5—183).—The influence of illumination on the dielectric constant selenium has been investigated in connexion with the fatigue ıd inertia of the element. It is shown in all selenium cells that ıe change in conductivity on illumination runs parallel with a ıange in capacity. The final capacity value and the final conıctivity are reached with similar inertia phenomena. The conducvity of the cells increases two- or three-fold on illumination, but ıe capacity increases only 5%. A cell which, with respect to its ›nductivity, exhibits fatigue, also exhibits the same phenomenon ith respect to its capacity. The dependence of the change in ıpacity on the intensity of illumination is much the same as that the conductivity. With increasing intensity of illumination, ıe sensitiveness of the capacity increases in a parabolic manner. he inertia on darkening the cell is greater than the inertia on lumination as far as the capacity effect is concerned, and, further, is considerably smaller in soft cells. The fatigue effect in soft ·lls on intense illumination is more marked, both with regard to ıe capacity change and the conductivity. The author has put ›rward an hypothesis of the mode of action of the selenium cell ıd has calculated the equilibrium of the cell for illuminated and ırk conditions. J. F. S.

**Fatigue of Alkali Metal Cells in the Neighbourhood of the ischarge Potential and the Influence of this on the Results f Photometric Measurements.** H. ROSENBERG (*Z. Physik*, 921, **7**, 18—64).—Sodium, potassium, and rubidium photoectric cells have been examined in connexion with the fatigue ffects often noticed in these cells. It is shown that these cells, hen filled as usual with an inactive gas, rapidly exhibit fatigue fects and also a rapid recovery. The effects are apparently not roportional to the intensity of the light or to the photoelectric urrent. In addition, slow changes of the sensitiveness of the ells are observed, which must be regarded as a type of fatigue ffect. The cause of tbe fatigue is found to be due to the adsorption f a positively charged layer of gas by the alkali metal, but it is

not decided whether electron absorption or a reduction of the field is the ultimate cause of the fatigue effect. The process appears to be intimately connected with the appearance of a powerful collision ionisation. The pure photo-effect is shown to be strictly proportional to the amount of light which has entered the cell. Taking into account these phenomena, a photometric process has been tested which leads to intensity ratios which are accurate to 0·1%. J. F. S.

**Equilibrium Law of Electrolytes.** K. JABLCZYŃSKI and F. J. WIŚNIEWSKI (*Roczniki Chemji*, 1921, **1**, 116—134).—The authors have deduced a dilution law of the form $n^{4/3}/n_0=k$ and have used this to calculate the value of $k$ for potassium, sodium, and lithium chlorides, using data obtained from cryoscopic measurements. It is shown that only in the case of potassium chloride is the value of $k$ constant, whilst in the case of the other two salts it may have even negative values. These facts are explained by hydration of the ions. Corrections which take into account the hydration have been introduced into van't Hoff's equation, and lead to a remarkably constant value for $k$ in all three cases; thus for potassium chloride $k = 3{\cdot}09$, for sodium chloride 3·10, and for lithium chloride 2·93. Furthermore, the number of molecules of water combined with the various ions has been calculated as follows: potassium, 0; sodium, 3; lithium, 11; chlorine, 0. Hydrochloric acid behaves in the same way as the salts mentioned, and when the hydrogen ion is taken as combined with nine molecules of water a very constant value, 4·74, is obtained for $k$. The equation has been applied to those weak electrolytes which apparently follow Ostwald's dilution law. The value of $k$ has been calculated for acetic acid from cryoscopic measurements and a remarkably constant value 0·00504 obtained, whereas the value of $k$ calculated from Ostwald's equation increases considerably with increasing concentration. On applying the equation to ebullioscopic data of solutions of the chlorides mentioned above, it is shown that the value of $k$ increases even more strongly than when cryoscopic data are used. This is explained by assuming that the ions are more heavily hydrated at 100° than at 0°. This is shown to be in keeping with facts. The value of $k$ at 100° is smaller than that at 0°, which shows that the degree of ionisation decreases with increase of temperature. This the authors attribute to a fall in the dielectric constant of water with increase of temperature. A rule has been deduced, in keeping with facts, which shows that the equilibrium constant of salts in aqueous solution is proportional to the dielectric constant of the solvent. J. F. S.

**Velocity of Sound in Air and Hydrogen at 0° and 1 Atm.** E. GRÜNEISEN and E. MERKEL (*Ann. Physik*, 1921, [iv], **66**, 344—364).—The velocity of sound in air is found to be 331·57 m./sec. and in hydrogen 1260·6 m./sec. The ratio of the specific heats for air is $C_p/C_v=1{\cdot}4034$ and for hydrogen 1·408, both at 0° and 760 mm. J. F. S.

**Specific Heats of Ammonia, Sulphur Dioxide, and Carbon Dioxide.** J. R. PARTINGTON and H. J. CANT (*Phil. Mag.*, 1922, [vi], **43**, 369—380).—The ratio of the specific heats $k=c_p/c_v$ for ammonia, sulphur dioxide, and carbon dioxide has been determined by a method depending on the relative velocities of sound in the gases and in air. The specific heats have been calculated using Berthelot's equation of state in all calculations. The following results were obtained at one atmosphere pressure: ammonia at 14·5°, $c_p/c_v$, 1·308, $C_p$ 8·77 cal., $C_v$ 6·70 cal.; sulphur dioxide at 13·2°, $c_p/c_v$, 1·290, $C_p$ 9·47 cal., $C_v$ 7·34 cal.; carbon dioxide at 20°, $c_p/c_v$, 1·303, $C_p$ 8·76 cal., $C_v$ 6·72 cal. J. F. S.

**Numerical Values of the Gas Constants.** F. HENNING (*Z. Physik*, 1921, **6**, 69—72).—The data on which the gas constant is based have been critically discussed and, on the basis of the most trustworthy experimental data, the value of this constant, in different units, has been calculated. The following values are recommended for general use as the most accurate, $R=0·08204\pm0·00003$ litre-atm./degree mol.; $R=(8·313\pm0·003)10^7$ erg/degree mol.; and $R=1·986\pm0·001$ $cal._{15°}$/degree mol. J. F. S.

**Theoretical Determination of the Chemical Constants of Monatomic Gases.** E. BRODY (*Z. Physik*, 1921, **6**, 79—83).—The author have deduced a mathematical expression for calculating the chemical constants of ideal monatomic gases on the basis of the first quantum theory and from statistical considerations. The expression obtained is the same as that deduced by Stern (A., 1919, ii, 219) and Planck (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 653). The expression has the form $C=\log_e(2\pi m)^{3/2}k^{5/2}/h^3$. J. F. S.

**Chemical Constants of Sodium and Potassium.** R. LADENBURG and R. MINKOWSKI (*Z. Physik*, 1921, **8**, 137—141).—The chemical constants of sodium and potassium have been calculated from existing data on the specific heat, vapour pressure, and latent heat of fusion of these elements. In the case of sodium, the value of the chemical constant $C$ is found to be 0·846, and on inserting this value in the equation $C=C_0+1·5\log M$, where $M$ is the molecular weight, the value of the constant $C_0$ is found to be $-1·20$ instead of $-1·59$, as in the case of mercury, argon, hydrogen, cadmium, and zinc. The data on which the calculation is based are analysed with the object of finding the cause for the discrepancy. In the case of potassium, the value of $C$ is found to be 1·016, which gives the value of $C_0$ as $-1·37$. J. F. S.

**Absolute Entropy and Chemical Constants.** MAX PLANCK (*Ann. Physik*, 1921, [iv], **66**, 365—372).—An answer to the criticism of Ehrenfest and Trkal (*ibid.*, 1921, **65**, 609) in which the difficulties in calculation of entropy experienced in the author's book ("Theorie der Wärmestrahlung," 1921) are pointed out. It is also doubted whether the equation $s=k\log W$, in which $W$ is the thermodynamic probability, will give the value of the entropy. The author answers the objections and criticisms and points out that they arise from a confusion of terms. J. F. S.

**Equation of Condition.** RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1921, 99, 361—382.)—A theoretical paper in which the equation of condition put forward by Wohl (this vol., ii, 117) is discussed and criticised. It is shown that this equation of condition leads to results which can scarcely be accepted; for example, the decrease of pressure at constant volume with increasing temperature in liquid systems, consequently this equation can have no theoretical significance. The critical point is always given by equations of condition which yield isotherms of the van der Waals form, by the coincidence of the three roots of the equation $v=f(p \,.\, T)$. The equality of four roots involves the introduction of a relationship between the constants; the equality of two roots leads to conditions which include, in addition to the critical point, also the maxima and minima. J. F. S.

**Physical Properties of Vapour–Liquid Systems. I.** WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 276—296).—Starting from relationships based on van der Waals's hypothesis of corresponding conditions, $\tau=T/T_c$ and $d_c/d=K=f(\tau)$. Where $T$, $d$, $T_c$, and $d_c$ are the temperature and corresponding density and $T_c$ and $d_c$ the same critical values, the author has deduced the following regularities from the experimental work of Young, Amagat, Mathias, Villard, Kamerlingh Onnes, and Crommelin. (1) The *value of K or log K increases with increasing molecular* weight of the liquid, and also when the liquid is associated. (2) Oxygen and argon have small values for $K$. In the case of associated liquids, it is shown that the concentration of non-associated molecules, $y$, is given by $y\%=100K/K_A$, where $K=d_c/d_p$ for a non-associated liquid and $K_A$ is the same ratio for an associated liquid at the same relative temperature ($\tau$=const.). The concentration of non-associated molecules in methyl alcohol and propyl alcohol increases proportionally to the temperature, but this is not true for ethyl alcohol. Ramsay's results for water and ethyl alcohol are satisfactory if it is assumed that the associated molecule of water contains three simple molecules and that of ethyl alcohol two simple molecules. The value of $K$ plays an important rôle in all cases where the physical state of a system liquid–vapour is characterised. The relationship between the surface tension $\gamma$ and the reduction of pressure below the meniscus in a capillary tube of radius $r$ is given by $(2\gamma/r\Delta f)_{\tau=\text{const.}}=K=\text{const.}$, and in the case of osmotic pressure $(P/\Delta f)_{\tau=\text{const.}}=K=\text{const.}$ The constant of Trouton's rule may be calculated by the equation $W_{\text{mol.}}=bR\log_e K=20{\cdot}4$, in which $R=2$ cal. $\log_e K=2{\cdot}303$, $\log_{10}K=2{\cdot}203\times2{\cdot}38$ or $2{\cdot}38$, depending on the ratio $K=d_c/d_p$ for the liquid at the relative boiling point $\tau=0{\cdot}65$ under a pressure of one atmosphere. J. F. S.

**Physical Properties of Vapour–Liquid Systems. II.** WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 297—304; cf. preceding abstract).—It is shown that over the range of relative temperatures $\tau=0{\cdot}50$ to $\tau=0{\cdot}95$ the expression $d_c^2/T\log_e K=B$ is constant, where $d_c$ is the density of the liquid, and $K$ the ratio $d_c/d_p$ in

which $d_v$ is the density of the vapour at the absolute temperature $T$. The deviations of $B$ never exceed a mean amount of $\pm 2\cdot 3\%$. A minimum value of $B$ is found between $\tau=0\cdot 85$ and $0\cdot 90$ and a maximum about $\tau=0\cdot 60$—$0\cdot 65$. Associated liquids are exceptional; these show a continual increase in the value of $B$ from $\tau=0\cdot 50$ to the critical temperature $\tau=1$. J. F. S.

**Vaporisation Coefficients of Solid and Liquid Mercury.** M. VOLMER and I. ESTERMANN (*Z. Physik*, 1921, 7, 1—12).—The authors have determined the velocity of vaporisation of mercury at temperatures from 59° to −180°. This demands the determination of the fraction, ($\alpha$), of the vaporised mercury which is condensed on a cooled surface, whilst the rest ($1-\alpha$) is reflected. It has been previously shown by Knudsen (*Ann. Physik*, 1915, [iv], 47, 697; 1916, **50**, 472) that at 19·45° $\alpha=0\cdot 95$, but at −140° $\alpha=1\cdot 00$. For the temperature range 59—0° the rate of vaporisation and consequently the value of $\alpha$ has been determined by measuring the rate at which a small globule of mercury deposited on the interior of the outside wall of a highly evacuated Dewar vessel filled with liquid air decreases. The Dewar vessel is kept in a thermostat at the required temperature during the experiment and the temperature of the bath up to 40° is taken as the temperature of the mercury, but for higher temperatures a correction is applied to the bath temperature to get the temperature of the mercury. This method is inapplicable at temperatures below 0° and above 60°. For these temperatures, 0° to −64°, the rate of vaporisation is determined by measuring the rate of change of the electrical resistance of the condensed film of mercury. A third method is also described which depends on the difference of readings in a graduated capillary tube due to vaporised mercury. The results show that for pure liquid mercury, irrespective of the temperature, the value of $\alpha$ is unity, but for solid mercury it is less than unity and decreases with decreasing temperature. It is shown that with sulphur, phosphorus, and benzophenone the value of $\alpha$ lies between 0·2 and 0·5. It is also shown that there is a close connexion between $\alpha$ and the extent to which a liquid may be supercooled. J. F. S.

**Coefficients of Vaporisation and their Relationship to Ostwald's Step Rule.** M. VOLMER and I. ESTERMANN (*Z. physikal. Chem.*, 1921, **99**, 383—394).—The coefficient of vaporisation, $\alpha$, has been determined for mercury over the temperature +59° to −64°, and found, for the liquid phase, to be equal to unity irrespective of the temperature. The known expression $G=1/\sqrt{2\pi R}\,.\,\sqrt{M/T}\,.\,p$ expresses actually the velocity of vaporisation for all temperatures: If this equation yields results for other substances similar to those obtained for mercury, then it becomes the first strictly true reaction velocity equation. In the case of solid mercury $\alpha$ is found to be approximately 0·9. The ratio $\alpha$ (solid)/$\alpha$ (liquid) has been determined for sulphur, phosphorus, and benzophenone and the values 0·3—0·4, 0·4—0·5, and 0·25 respectively have been obtained. The Ostwald step rule and the

limits of its applicability to the separation of the liquid and sol phases from the vapour condition are shown to be due to tl different α-values of the solid and liquid phases. J. F. S.

**The Separation of Miscible Liquids by Distillation. I** ARTHUR FELIX DUFTON (T., 1922, **121**, 306—308).

**Divergences of the Value of the Mechanical Equivalent ‹ Heat.** WOJCIECH SWIENTOSŁAWSKI (*Roczniki Chemji*, 1921, : 171—177).—The author gives a short description of facts whic show that the value of the mechanical equivalent of heat require exact verification. It is shown to be probable that the value obtained by electrical and mechanical methods are not in agree ment. The measurements of Jaeger and Steinwehr show that i bomb calorimetry conditions often exist which increase the amoun of heat obtained by the introduction of electrical energy into calorimeter. It is also pointed out that adiabatic calorimetry ha not been employed in the measurement of this constant. J. F. S.

**Heat of Vaporisation of Sodium and the Probability of th Transition of the Sodium Atom from the Resonance to th Normal Condition on the Basis of Optical Measurements** R. LADENBURG and R. MINKOWSKI (*Z. Physik*, 1921, **6**, 153—164).—The authors have measured the magnetic rotation of th plane of polarisation in the immediate neighbourhood of the *1* line by the method described by Senftleben (*Ann. Physik*, 191[ [iv], **47**, 949) at various temperatures of the emitting vapou The sodium used was contained in an air-free glass tube in a electric furnace the temperature of which was constant to ±0·1' It is shown that the dependence of *N* (the number of electron which vibrate with the atoms) on the temperature can be regarde as a relative vapour pressure curve, if the theory that *N* is pro portional to the number of sodium atoms present is accepted Calculation from the experimental results leads to the value fo the heat of vaporisation of sodium $l_{T=0}=25·9$ Cal. This value i probably uncertain to about 2%. J. F. S.

**Action of Forces between Separated Atoms in Diamon and Aliphatic Molecules.** K. FAJANS (*Z. physikal. Chem.*, 1921 **99**, 395—415).—A theoretical paper in which it is shown that i in analysing the results of heat of combustion experiments th assumption is made, as a first approximation, that only neigh bouring atoms have a noticeable energetic action on one another then it appears that the firmness of a C–C linking in the diamond is somewhat greater than that in aliphatic hydrocarbons. Fron this it follows that the heat of combustion of hydrocarbons witl branched chains should be somewhat smaller than that of th straight chain isomerides, a conclusion which is in keeping witl experimental data. To explain the above relationships it i assumed, (1) that the energy of the C–C linking in aliphatic sub stances and diamond is constant, irrespective of whether or nc the carbon atom is bound to further carbon atoms or also with hydrogen. (2) That separated and distant atoms have a notice-

able energetic action on one another. As a second approximation in the quantitative analysis, only those linkings which lie on a common edge of the tetrahedron are considered. From a comparison of diamond with the hydrocarbons the relationship $y_m - 2x_m + h \sim 1-2$ Cal., between the energies of the three types of edge linkings (C–C, C–H, H–H), where $y_m$, $x_m$, and $h$ are respectively the energies of formation of the three types of linking. This relationship indicates a method of explaining the difference in properties of the chain isomerides and also the exceptional position of the first member of homologous series. In the case of aliphatic hydrocarbons, alcohols, ketones, and esters of monobasic acids, the chain isomerides with low boiling point and heat of vaporisation possess a lower heat of combustion, a stronger saturation of the forces in the molecule corresponding with a weaker intermolecular force. The difference in the boiling points and the specific heats of the chain isomeride is therefore brought into relationship with the difference in the intramolecular energy, and the latter is attributed to the mutual action between separated and distant atoms. J. F. S.

**The Meaning of the Atomic Constants of Heat of Combustion and Molecular Refraction.** WALTER HÜCKEL (*J. pr. Chem.*, 1921, [ii], **103**, 241—248).—A theoretical paper, in which the author states the various relations that have been found by Steiger (A., 1921, ii, 473) and others between the various "atomic" and "linking" constants of organic compounds and of the elements forming them, and points out some relations that seem to follow.
W. O. K.

**New Data in the Thermochemistry of Organic Substances.** WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, **1**, 305—315).—The heat of dissociation of hydrogen, chlorine, bromine, iodine, and solid carbon into individual atoms, determined during recent years, has been used to obtain the value of the constant $\epsilon$ of the equations (C—I)=(H—I)+$\epsilon$—3; (C—Br)=(H—Br)+$\epsilon$—3; (C—Cl)=(H—Cl)+$\epsilon$; (C—C)=(H—C)+$\epsilon$; (C—N)=(H—N)+$\epsilon$; (C—S)=(H—S)+$\epsilon$+2; (C—O)=(H—O)+$\epsilon$+5; (C—H)=(H—H)+$\epsilon$+15. The symbols (C—I), (H—I) indicate the heat of formation of the single link between the atoms named. When the values 81·3 Cal., 106 Cal., 46 Cal., and 36 Cal. are taken as the heat of formation of the molecules of hydrogen, chlorine, bromine, and iodine, respectively, as represented by $2X - = X_2 + Q$ Cal., and the heat of formation of solid diamond as $-\overset{|}{\underset{|}{C}}- = C_{sol} \times 287$ Cal., it is possible to calculate the heat of formation of the links (C—C) and (C—H). According to Fajans (A., 1920, ii, 354), *(C—C)=137·5 Cal. and (C—H)=117·0 Cal.* Using the above data in the equations, a mean value of 20·6 is obtained for $\epsilon$. From the heat of formation of the linkings (H—Cl)=115·5 Cal., (H—Br)=72·0 Cal., (H—I)=52·7 Cal., it is shown that (C—Cl)=136·3 Cal., (C—Br)=89·7 Cal., and (C—I)=70·3 Cal. An analysis of the above results shows that the heat of formation of a link is an additive

quantity made up of parts due to the links of the atoms concerned These parts have been calculated as follows: (C—)=68·8 Cal. (H—)=48·2 Cal., (Cl—)=67·4 Cal., (Br—)=23·8 Cal., (I—)=4· Cal. The heat of formation of a link between two atoms is th sum of the two atomic values. This regularity is probably existen in inorganic compounds also, for if the above atomic values of th halogens are subtracted respectively from the heat of formation o the corresponding haloids of potassium, the value of (K—) i found to be 91·2, 94·5, and 93·7 Cal., and by the same method th value for sodium (Na—) is 83·3, 84·0, and 82·7 Cal. J. F. S.

**Heat of Coagulation of Ferric Oxide Hydrosol with Electro lytes.** FREDERICK L. BROWNE and J. HOWARD MATHEWS (*J Amer. Chem. Soc.*, 1921, **43**, 2336—2352).—The heat of coagulatio of ferric oxide hydrosol of various concentrations and purity b various concentrations of sodium oxalate, sulphate, chloride, an hydroxide, potassium ferricyanide, and sulphuric acid has bee determined. It is shown that the dilution of ferric oxide hydrosol of varying purity is accompanied by measurable heat effects unt the purity exceeds 21 or 22 (the ratio of gram equivalents of ferri oxide per litre to gram equivalents of chlorine per litre is terme the purity of the sol), beyond which point the heat of dilutio is zero. If the heat of dilution per gram-equivalent of chlorine i the sol is plotted against the chlorine content, the curve is of th same nature as that for the heat of dilution of ferric chloride solution of varying concentration. The thermal behaviour of ferric chlorid solutions on dilution confirms the observations of Goodwin (*Physica Rev.*, 1896, **9**, 251; 1900, **11**, 193), to the effect that the hydrolysi of ferric chloride takes place in two steps, the first an instantaneou and the second a slow reaction. The mixing of ferric chlorid solutions with common electrolytes involves very significant hea changes. The heats of coagulation have been reduced to curve showing the heat of coagulation as a function of the purity whic vary widely in shape with the nature of the coagulant; the hea effect is usually positive, but with sodium sulphate and sodiur chloride at low purities it is negative. As the purity increases, th heat of coagulation becomes smaller, and finally becomes negligibl except in the case of sulphuric acid. The peculiar behaviour c this last electrolyte is due to solution of the ferric oxide. Whe the heat of coagulation is plotted against the concentration of th coagulating electrolyte, smooth curves are obtained which sho no break at the point of limiting concentration. The heat effect observed on coagulating ferric oxide sols with electrolytes are t be attributed to the action of the electrolytes in the coagulants o the electrolytes, particularly ferric chloride, present in the so The change in dispersity of the ferric oxide on coagulation does no involve a greater heat change than 1—2 cals./gram-equivalent c ferric oxide. In the case of ferric oxide hydrosols, there is n heat of peptisation analogous to the heat of solution of crystalloid J. F. S.

**Kation Volumes in Permutite.** RICHARD LORENZ (*Z. Physil* 1921, **6**, 269—270).—A criticism of the work of Günther-Schulz

ı the determination of the kation volumes in permutite (A., 1921, , 624). It is pointed out that the value found for the alkali ion is ractically the same as that of the alkali atom. It is suggested ıat the alkali ions in permutite fill only a small amount of the ›ace and have a large space to vibrate in. This great mobility characteristic of permutite. The kation radii calculated by ünther-Schulze are probably too large, for the new determinations Fajans and Herzfeld and also those of Landé are much smaller ıd lie very close to those calculated from the ionic mobility by orenz and Born. J. F. S.

**The Velocity of Extension of Thin Layers of Oils on the urface of a Sheet of Water.** PAUL WOOG (*Compt. rend.*, 1922, 74, 162—165).—For fatty oils, where all the molecules intervene, .e velocity of extension is practically proportional to the ratio he carboxyl groups of the glycerides+the douhle linkings+the idity)/viscosity. In mineral oils, however, the velocity of tension depends only on the unsaturated molecules, which are w in number, and hence the viscosity plays an insignificant part. ı mixtures of the two types of oil, the results depend on the relative oportions in which the active fatty oil and the comparatively active mineral oil are mixed. W. G.

**High Pressure Due to Adsorption.** WILLIAM D. HARKINS ıd D. T. EWING (*Chem. News*, 1922, **124**, 23—24, 31—35).—Cf. is vol., ii, 123. J. F. S.

**Electro-adsorption as a Purely Chemical Process.** I. M. OLTHOFF (*Kolloid Z.*, 1922, **30**, 35—44).—The author discusses ectro-adsorption (adsorption of ions) and from the experi-ental results of Freundlich, Odén, and others shows that the ocess is strictly a chemical one. The adsorption of copper, lead, orphine, codeine, papaverine, atropine, ferricyanide, oxalate, romate, and iodate ions by norit carbon confirms this view. is shown that the adsorption isotherm can be deduced directly om the stoicheiometric relationships, if it is assumed that the ectro-adsorption is a process in which a sparingly soluble sub-ance, contained in the adsorbent, is converted by the adsorbed n into another sparingly soluble substance. The coefficient $1/n$ the adsorption isotherm bears a direct relationship to the valency the reacting substances. If $1/n$ is equal to $a$ for a univalent ion, en it has the value $a/2$ for a bivalent ion and $a/3$ for a tervalent ı. This relationship is confirmed by the present experiments d by the earlier work of Freundlich and Odén. The significance the quantity of the adsorbent is explained by the characteristic nstitution of its surface layer of particles. The active ion, which termines the charge in the surface layer, and in adsorption rms the insoluble salt, is present in this layer in far larger concen-ıtion than in the liquid. When equilibrium has been set up on e surface of a particle, then the concentration of the active ion, contact with the excess of reacting ions, is small. In such a se, if fresh adsorbent is placed in the liquid, then the reacting ions

are again in contact with large concentrations of active ions, and the reaction commences anew. The general chemical theory in its relationships to colloid chemistry is shortly discussed. J. F. S.

**Origin of the Charge of a Colloidal Particle and its Neutralisation by Electrolytes.** JNANENDRA NATH MUKHERJEE (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 103—115).—The charge of a number of suspensoids has been shown to be due to the adsorption of a common ion and the nature of the chemical forces which cause this adsorption has been defined. The effect of the electrical charge of a surface (due to the disorption of ions) on ions of opposite sign has been theoretically investigated for the case when chemical action does not take place between the surface and the ion. It has been shown that the electrical forces are sufficiently strong to account for adsorption. The stability of the adsorption of an ion of opposite sign by electrical forces has been given a quantitative form, assuming that the charge of the surface consists of ions which can be treated as point charges widely separated from each other. Actual calculations justify this assumption. The reversal of the charge by electrical adsorption has been discussed. The following *series of the adsorbability of kations by a negatively charged* surface has been deduced from the theory: $Th^{\cdot\cdot\cdot\cdot} > Al^{\cdot\cdot\cdot} > Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Ca^{\cdot\cdot} > Mg^{\cdot\cdot} > H^{\cdot} > Cs^{\cdot} > Rb^{\cdot} > K^{\cdot} > Na^{\cdot} > Li^{\cdot}$. This order is the same as that of the precipitating power of these ions for a number of suspensoids of widely differing chemical properties. Equations deduced from the theory agree satisfactorily with the experimental observations of Elissafoff (A., 1912, ii, 419) on electro-endosmosis. The chemical affinity of the surface atoms is not always negligible, and for this reason the series given above cannot be expected to hold in all cases. J. F. S.

**Electrical Theory of Adsorption.** W. HARRISON (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 116—118).—A criticism of Mukherjee's theory of adsorption (cf. preceding abstract). The author is of the opinion that the double layer consists of a surface of rigidly fixed atoms under continuous bombardment of positively and negatively charged ions, any particular point on the rigid surface becoming in turn negative, neutral, and positive, these conditions arising in any order. The observed contact difference is the average effect of these conditions. When several kinds of atoms are present in the solution, the average number of any one of them at the surface will depend on their concentration, valency, and mobility. The variation of contact difference from negative to neutral and positive was observed with cotton and aluminium sulphate near the neutral point (*J. Soc. Dyers and Col.*, 1911, **27**, 279; 1918, **34**, 91). These variations occurred during the same experiment, the readings being direct measurements of *E.M.F.* developed by filtration under pressure. J. F. S.

**Diffusion of Hydrogen through Iron and Platinum.** GERHARD C. SCHMIDT and TH. LÜCKE (*Z. Physik*, 1921, **8**, 152—159).—The diffusion of hydrogen through iron and platinum has

been investigated. A sheet of the metal was fixed between two glass vessels, hydrogen was electrolytically generated on one side of the sheet and the potential on the other side measured over a period of time up to about twenty-four hours. The metal sheets were of various thicknesses. It is shown in the case of iron that the passage of the hydrogen through the metal is always indicated by a fall of potential. In the case of thin sheets, the fall of potential is observed as soon as the electrolysis commences; the fall of potential is rapid at first, and gradually becomes slower until, when the liberation of hydrogen has proceeded for some time, it becomes constant. With sheets of medium thickness (0·5—1·0 mm.) the fall of potential is gradual, and with sheets thicker than 1·0 mm. there is no fall of potential. On breaking the polarising current, the potential increases, the more quickly the thinner the metal. From this fact it is deduced that the hydrogen diffuses into the liquid. With thicker sheets, the increase of potential is slower, which is explained by the longer time required for the relatively large volume of hydrogen to diffuse into the liquid. Similar results are obtained in the case of platinum. The results show that the passage of hydrogen across platinum plates is a diffusion and not, as stated by Nernst and Lessing (*Göttinger Nachr.*, 1902, 146), due to small pores in the metal. The Nernst-Lessing rule was shown by them to hold for palladium and thin sheets of platinum, but not for thicker sheets of platinnm. It is shown that the reason for the rule holding with palladium is that on account of the great power of palladium for absorbing hydrogen practically none is liberated from the other side, and consequently the condition of the rule is obtained. J. F. S.

**Dispersoid Analysis of Non-aqueous Systems.** WOLFGANG OSTWALD (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 89—93).—The author describes the preparation of membranes and jellies suitable for dispersoid analysis of solutions in alcohol of 97%, for both dialysis and diffusion experiments. The mercury sulphide alcosol, the preparation of which is explained, is an especially stable sol suitable for these tests. Solutions of dyes, resins, neutral salts, fatty acids, and soaps, as far as at present examined, produced by the spontaneous solution of these substances in 97% alcohol, are all molecular-dispersed, or contain, at any rate, molecular-dispersed particles in considerable proportions. Zein, the protein of maize which is soluble in alcohol, is also found to be dialysable. J. F. S.

**Solubility. III. Solubility of Metal Ammonia Salts in Salt Solutions.** J. N. BRÖNSTED and AGNES PETERSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 2265—2292; cf. A., 1920, ii, 536).—A long list of the solubilities of eighty-six cobalt, chromium, and rhodium complex ammine salts in water at 0° and 20° is given in the paper. The solubilities of a large number of complex ammine salts of cobalt and chromium in solutions of potassium chloride, formate, chlorate, trichloroacetate, dichloroacetate, monochloroacetate, thio-

cyanate, hydroxide, nitrate, and phthalate; sodium chloride, sulphate, chlorate, nitrate, formate, oxalate, and benzenesulphonate; magnesium sulphate and chloride; calcium formate, acetic acid; and mono-, di-, and trichloro-acetic acids of various concentrations have been determined at 0°. In the preceding papers (*loc. cit.*) it was shown that the expression log $S/S_0=a(C_t^{1/3}-S_0^{1/3})$ represents approximately the solubility changes of salts in hetero-ionic solvents up to about 0·1*N*-solutions, when *a* is a constant which for uni-univalent salt systems has the value 1/3, *C* is the concentration of the solvent salt, $S_0$ the solubility in water, and *S* that in the salt solution at the same temperature. The experimental data furnished for salts of the same type in the present paper agree approximately with the formula, and an equation of the same type is found for bivalent salts. The individual nature of the salts employed is more pronounced in the larger amount of material now presented and tends to obscure any numerical regularity in salt systems of promiscuous types. The experiments lead to the following rules. The infinence of the solvent increases with increasing valency of the ion of the solvent salt, which, in the case of ter-bivalent salts, leads to an enormous increase of solubility, even on the addition of solvents of very low concentration. When both the dissolved and dissolving ions are of higher valency, the effect of the sign of the electric charge is very marked, producing the highest solubility values when the multivalent ions of solvent and solute are of different sign. The reason for the appearance of individuality in the solubility curves is to be sought partly in the hydration of the solvent and the solute, and partly in the fact that in these ions the mass is not to be regarded as a point, but as a particle of varying size bearing a number of electric charges of opposite signs, the algebraic snm of which gives the valency of the ion. It is probable that the size of the ion in the present cases will have an influence of considerable magnitude. J. F. S.

**Probability of Spontaneous Crystallisation of Supercooled Liquids.** C. N. HINSHELWOOD and HAROLD HARTLEY (*Phil. Mag.*, 1922, [vi], **43**, 78—94).—The statistical investigation of the spontaneous crystallisation of supercooled salol, phenol, *p*-toluidine, and *o*-nitrophenol leads to the following conclusions: In all these cases crystallisation is provoked by colloidal organic dust particles, the activity of which diminishes in general as the result of heating or ageing. The effectiveness of the dust particles depends on their radius. If this is equal to the radius of a small particle of the solid which should thermodynamically be in equilibrium with the supercooled liquid, then crystallisation occurs at once. If the radius is less than this, the supercooled liquid has an average life depending on the discrepancy between the equilibrium radius and the radius of the particles present. The magnitudes of these quantities are discussed. The results of crystallisation experiments are given: 16 sets of 70 tubes of salol were kept at 32·3° in a thermostat and the number which had crystallised at various times noted; similar results are recorded for 12 sets of 41 tubes of phenol at 18—25°;

8 sets of 122 tubes of *p*-toluidine at 33·36—17·48° and 5 sets of 130 tubes of *o*-nitrophenol at 38·72—31·1°. J. F. S.

**Structure of [Hanging] Drops of Mixed Liquid Crystals.** O. LEHMANN (*Ann. Physik*, 1921, [iv], **66**, 323—343).—The structure of hanging drops of liquid crystals of *p*-hydroxyphenetole and cholesteryl benzoate has been examined between parallel Nicols by means of the dichroic effects produced. A number of diagrams and descriptions of the structure observed are included in the paper. J. F. S.

**Submicrons Visible in the Tyndall Cone to the Naked Eye.** J. TRAUBE and P. KLEIN (*Kolloid Z.*, 1922, **30**, 19—20).—When 30 c.c. of 1/30000 *N*-lead nitrate solution are treated with 2 drops of *N*/2-sodium carbonate solution in a rectangular vessel, stirred, and illuminated by a Tyndall cone, it is found that in forty to sixty seconds an extremely large number of small particles are visible by means of a hand lens. The particles are in violent and irregular motion. As the time of the existence of these particles increases more and more light is reflected from them, so that in about two minutes they are visible to the naked eye at a distance of 2 metres. It is held that the particles are crystals and are visible on account of their rotation, which causes an intermittent reflexion of light from the crystal faces. The phenomenon is not produced by all concentrations of lead nitrate, *N*/10000 is too concentrated and *N*/70000 is too dilute; the best concentration is that given above. The same phenomenon may be observed with very dilute solutions of calcium sulphate, calcium ammonium phosphate, barium sulphate, mercurous chloride, and lead chloride. J. F. S.

**Fibrous Structure of Hard Drawn Metal Wires.** M. ETTISCH, M. POLANYI, and K. WEISSENBERG (*Z. physikal. Chem.*, 1921, **99**, 332—337).—From the *X*-ray examination of hard and soft wires of copper, tungsten, iron, molybdenum, palladium, aluminium, silver, and zinc, it is shown that the crystallite in soft wires is arranged irregularly, whilst in hard wires it is arranged regularly. In the case of the metals with a space centred cubic lattice (tungsten, iron, molybdenum), it is found that only a single lattice plane lies in the section of the wire, namely, the plane (110), whilst in the case of the metals with a face centred cubic lattice (copper, palladium, and aluminium) two lattice planes lie in the section of the wire, namely, the planes (111) and (100). The crystallite arrangement in hard wires is termed a fibrous structure because this arrangement was first observed in natural fibres such as ramie and silk. J. F. S.

**Molecular Structure of Amorphous Solids.** C. V. RAMAN (*Nature*, 1922, **109**, 138—139).—In view of the fact that glass exhibits a very strong scattering of light, its magnitude being of the order that might be expected if the arrangement of the molecules

was irregular, it is assumed that such is the case. If the arrangement of the molecules approximated to the crystalline state, the scattering of light would be merely that due to the thermal movements of the molecules, and would be much smaller. Careful microscopic examination failed to disclose any inclusions, to which the effect has previously been ascribed (Strutt, *Proc. Roy. Soc.*, 1919, [*A*], **95**, 476). A. A. E.

**Action of Penetrating Radium Radiation on Inorganic and Bio-colloids. III.** A. Fernau and Wo. Pauli (*Kolloid Z.*, 1922, **30**, 6—13; cf. A., 1915, ii, 722; 1917, ii, 189).—A continuation of previously published work (*loc. cit.*). In the present paper the influence of the radiation from a radium preparation equivalent to 78·6 mg. of radium on gelatin, albumin, casein, acid albumin, and lecithin has been investigated. Of the radiation emitted by the radium preparation, only 25% of the hardest β-radiation and 99% of the γ-radiation came in contact with the colloids. It is shown that the viscosity of a 0·99% solution of glutin from bone glue at 35° falls rapidly at first under the influence of the radiation and then successively less rapidly, but in the presence of 0·1*N*-sodium chloride the fall in viscosity is much slower. The addition of 0·01*N*-hydrochloric acid to 0·5% glutin solution causes at first a rapid fall in the viscosity, which becomes less rapid as the time increases. Under the action of the radiation, the rate of fall of the viscosity is still more rapid. The action of the radiation is analogous to the action of heat on glutin. Glutin jellies when exposed to the radiation liquefy, but the portion nearest the tube containing the radium sets to a solid, opaque mass which sticks to the tube and is insoluble in water, although soluble in alkali hydroxide. The coagulation of serum-albumin, which had been freed from globulin, by the radiation is found less rapid in the presence of sodium chloride, the retardation being greater the greater the concentration of the salt. The time required for coagulation of albumin depends on the concentration of the albumin; it decreases at first with increasing concentration, passes through a minimum at 0·5—1·0% of albumin, and then increases. The action of the radiation on solutions of the sodium salts of acid albumin and casein is to displace the equilibrium toward the acid side, that is to decrease the concentration of the hydroxyl ion. Thus an acid albuminate, prepared from serum-albumin, had a hydroxyl-ion concentration $1{\cdot}66 \times 10^{-5}N$; after subjection to the radiation for a week the value was $1{\cdot}57 \times 10^{-6}N$, and after three weeks $3{\cdot}62 \times 10^{-8}N$, whilst sodium caseinate solution had the value $8{\cdot}64 \times 10^{-6}$, which became $1{\cdot}19 \times 10^{-6}$ after treatment with the radiation for a week. A solution of 3 grams of lecithin in 200 grams of water exhibited at 25°, under the action of the radiation, a gradual fall in viscosity, but scarcely any change in the hydrogen-ion concentration or in the specific conductivity. Similar results are also found with a 0·2% emulsion of cholesterol. The results show that whilst albumins undergo considerable change under the action of radium radiation, this is not the case with lipoid emulsions. J. F. S.

**Protective Colloids. XI. Carragheen as a Protective Colloid. I. General Colloid-chemical Investigation of the Extract of Irish Moss.** A. Gutbier and J. Huber (*Kolloid Z.*, 1922, **30**, 20—31; cf. A., 1921, ii, 537).—The method of preparation and properties of colloidal solutions prepared from Irish moss are described. Purified carragheen (30 grams) is placed in a litre of water at the ordinary temperature and kept until the swelling process is complete, then it is vigorously shaken for five hours. The mucilage is separated by pressing through linen. Several other preparations are described; the amount of dry colloid varies between 0·4400 gram and 0·2100 gram per 100 c.c. of mucilage, and the ash between 0·0246 and 0·0600. Dialysis reduces the amount of ash and removes the turbidity and the foul odour and raises the degree of dispersion. Carragheen solutions do not produce fungoid growths when kept, and it is therefore unnecessary to add stabilising agents. On keeping, the viscosity of a 0·55% mucilage fell from 15·29 to an approximately constant value of 7·19 in thirty-three days. The rate of decrease in viscosity is rapid at first and subsequently much slower. The change in viscosity with ageing indicates the change of the mucilage to a more stable system. Boiling the mucilage reduces the viscosity by an amount which increases with the length of time of boiling. This indicates a change in the chemical constitution of the mucilage, but after filtration no further change occurs on prolonged keeping. Heating therefore may be regarded as a hastened ageing and gives rise to stable colloidal solutions. The viscosity increases with increasing concentration, but the amount of increase is greater the higher the temperature employed in the preparation. Electrolytes have no unfavourable action on the mucilage, no coagulation or visible change being brought about except in the case of sodium hydroxide, where it becomes light brown in colour. Increasing concentration of hydrochloric acid, sodium hydroxide, and sodium chloride decreases the viscosity to values which approach a constant valne as the concentration of the electrolyte increases. J. F. S.

**Protective Colloids. XI. Carragheen as Protective Colloid. II. Colloidal Silver.** A. Gutbier, A. Wolf, and A. Kiess (*Kolloid Z.*, 1922, **30**, 31—35; cf. preceding abstract).—Extract of Irish moss prepared as indicated previously (*loc. cit.*) has been investigated as to its efficacy as a protecting colloid in the case of colloidal silver. Before use, the mucilage is aged for a considerable time and thereby stabilised. Colloidal silver prepared in the presence of carragheen by hydrazine hydrate has colours varying from dark reddish-brown to brownish-yellow in transmitted light, depending on the concentration of the silver nitrate used. It is exceedingly stable and remains unchanged for two months, and may be evaporated to dryness on a water-bath to an almost black residue which is completely reversible. On the other hand, evaporation in a vacuum over sulphuric acid yields a viscous paste which is not completely reversible, but yields a secondary system with water which is only stable in dilute solutions. Colloidal

solutions of silver have been prepared in the presence of carragheen with a concentration of 17% of silver, but they were not very stable. Carragheen itself has a reducing action on silver nitrate and produces colloidal silver. This action is not complete, but the percentage of reduced silver increases with the dilution of the silver nitrate; thus *N*/10-silver nitrate gives 8·98% of reduced silver, whilst *N*/640-silver nitrate gives 58·54% of reduced silver, the amount of carragheen being the same in all cases. J. F. S.

**Ultra-violet Spectroscopical Studies on the Antagonistic Action of Salts in Organic Colloidal Solution.** TETSUTARO TADOKORO (*J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 37—49; cf. A., 1918, ii, 432).—The effect of different salts on the degree of dispersion of organic colloidal solutions (egg-albumin, taka-diastase blood-serum, and lettuce juice) was studied by observing the change induced in their absorption spectra in the ultra-violet. Certain pairs of salts were shown to have antagonistic effects on dispersion Ultramicroscopic observations confirmed the conclusions drawn from the spectroscopical observations. G. W. R.

**The Importance of Imbibition for some Biochemical Problems.** M. RICHTER-QUITTNER (*Biochem. Z.*, 1921, **121** 273—292).—By means of the Zsigmondy-Haen ultra-filtration apparatus, the author has examined the influence of electrolytes and non-electrolytes on the velocity of ultra-filtration of various dispersoid systems, for example, sera, for substances which inhibit imbibition will accelerate filtration. All potassium salts, heavy metal salts, urea, and sugar inhibit, whilst other kations favour imbibition. For anions the Hofmeister series holds good. H. K.

**Reversal of Phases in Emulsions and Precipitation of Suspensoids by Electrolytes.** SHANTI SWARUPA BHATNAGAR (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 27—31).—A study of the reversal of phase in oil–water emulsions in the presence of pure soaps by electrolytes (cf. T., 1920, **117**, 542), and the precipitation of arsenic sulphide sols by lithium chloride (Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2030). It is shown that the power of ions in reversing the phases in oil–water emulsions in the presence of soap follows the order: $Al^{\cdot\cdot\cdot} > Cr^{\cdot\cdot\cdot} > Ni^{\cdot\cdot} > Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Ca^{\cdot\cdot}$. The amount of electrolyte required varies with different soaps but the order of the different electrolytes remains the same. The greater the dilution, that is, the distance between the oil particles in an emulsion, the larger the amount of a multivalent ion required to bring about reversal of the phases. Some measurements are given of the effect of diluting milk on the rate of coagulation by dilute sulphuric acid. It is shown that the greater the dilution the larger is the concentration of acid required to bring about an immediate coagulation. Soaps are regarded as exerting a protective action on oil–water emulsions, and it is shown that the protective action follows the order: potassium stearate > sodium stearate > sodium and potassium oleate > potassium oleate > sodium oleate.

J. F. S.

**Peptisation and Precipitation.** N. G. CHATTERJI and N. R. )HAR (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 122—127).—Silver hloride, silver chromate, calcium silicate, cupric fluoride, and arium sulphate when precipitated in the presenee of glycerol or ɔncentrated sucrose solutions are not peptised. The hydroxides f iron, nickel, cobalt, thorium, and mercury may be peptised by dding an alkaline hydroxide to the solutions of salts of these metals ı the presence of glycerol or concentrated sucrose solution. In the ase of gold or uranium salts, ammonium hydroxide should be used ıstead of sodium hydroxide. In these cases, peptisation can only e brought about if the alkali is added to the mixture of the salt nd glycerol, but precipitation takes place if the solution of the salt ı added to the mixture of glycerol and alkali. These results are ıpported by conductivity measurements. The major portion of ıe hydroxides of aluminium, chromium, lead, mercury, and copper, ·hen dissolved in sodium or potassium hydroxide, exists as a colloid, ·hilst zinc hydroxide mainly forms a zincoxide, as shown by conuctivity experiments. Similarly, the hydroxides of aluminium, ·on, and chromium form colloidal solutions in acetic acid, whilst nc hydroxide forms zinc acetate. The transformation of the lue hydroxide of copper to the black variety and that of the blue ydroxide of cobalt to the pink form are changes of the same type, ıd are almost equally effected by different catalysts. The hydrxides of aluminium, chromium, and zinc respectively are adsorbed y ferric hydroxide when the latter is precipitated in the presence f solutions of the hydroxides of these metals in potassium hydroxide.

J. F. S.

**A Kinetic Precipitation Measurer.** WO. OSTWALD and .-V. VON HAHN (*Kolloid Z.*, 1922, **30**, 62—70).—Two new precitation measures are described, which permit of the precipitation ·ocess and the peptisation of colloidal solutions being studied ınetically. The one instrument, the two-limbed measurer, is ısed on the principle of level difference in communicating tubes, ıd the change of this difference due to decrease of density of one quid by the sedimentation of the disperse phase contained in it. The cond apparatus, the single-limbed measurer, depends on the rise of ıe seal liquid column of an enclosed gaseous volume, through change the density of the seal liquid in consequence of the precipitation the disperse phase which it contains. A number of examples of e use of these instruments in the kinetic measurement of the ·ecipitation processes of typical sols are given. J. F. S.

**Distribution of certain Drugs between Immiscible Solvents.** '. O. EMERY and C. D. WRIGHT (*J. Amer. Chem. Soc.*, 1921, **43**, !23—2335).—Distribution experiments between water and chlororm have been carried out with caffeine, antipyrine and *p*-acetoxy·etanilide. It is shown that the most suitable temperature for the :traction of caffeine from water by chloroform is the ordinary mperature, although a change of temperature from 12° to 40° only duces the amount recovered from water by a single extraction ɔm 96·3% to 93·2%. The distribution is the more favourable to

the chloroform the more dilute the aqueous solution. The effect of small concentrations of sodium hydroxide, sodium acetate, sulphuric acid, sodium salicylate, sucrose, alcohol, and citric acid on the distribution of caffeine between water and chloroform has been examined at 25°. The presence of sulphuric acid leads to a less efficient extraction of the caffeine, whilst sodium salicylate reduces the amount extracted from 96% to 20·7%, due in all probability to the formation of a molecular compound between caffeine and sodium salicylate. The solubility of caffeine in water, and aqueous solutions of sulphuric acid (*N*), citric acid (*N*), potassium bromide (*N*) and (2·5*N*), sodium salicylate (*N*) and (0·1*N*), sodium benzoate (*N*) and (0·1*N*) has been determined at 25°. The solubility in grams per 100 c.c. of solvent is 2·071 in water, 3·355 in sulphuric acid, 6·411 in citric acid, 2·136 and 2·035 respectively in potassium bromide, 22·22 and 4·921 respectively in sodium salicylate, and 15·27 and 3·422 respectively in sodium benzoate. The solubility determinations and cryoscopic measurements of mixtures of caffeine with sodium salicylate and sodium benzoate respectively confirm the complex salt formation with these salts. Distribution experiments of caffeine between absolute chloroform and water, *N*-sulphuric acid, *N*-potassium bromide, 0·1*N*-sodium salicylate, and 0·1*N*-sodium benzoate have been made at 25°. It is shown that potassium bromide has but little effect on the partition, whilst sodium salicylate reduces the amount of caffeine recovered from the water solutions by the greatest amount. The distribution of antipyrine shows that there is no tendency to the formation of double salts with sodium salicylate, but, on the other hand, there is a far greater depression in the percentage of antipyrine extracted from *N*-sulphuric acid, when compared with that from pure water solution, due presumably to difference in basicity. In the case of *p*-acetoxyacetanilide, somewhat lower distribution ratios are obtained than for either caffeine or antipyrine. The solubility of *p*-acetoxyacetanilide in water at 25° is found to be 0·239 gram per 100 c.c. of water, and in chloroform at the same temperature 3·250 grams in 100 c.c. of chloroform. J. F. S.

**Theory of the Liesegang Rings.** MARTIN H. FISCHER and GEORG D. MCLAUGHLIN (*Kolloid Z.*, 1922, **30**, 13—16).—It is shown that Liesegang rings are only observed when a liquid phase is present; they may be formed when two dissolved substances, which react with one another, are brought together in the presence of a third insoluble substance; the formation of the rings occurs on the side of the solution of lower concentration, the rings tend to increase in thickness from the commencement of their formation and during the growth tend to pass from the originally liquid and amorphous condition to the solid and crystalline form. All substances which give satisfactory Liesegang rings are impermeable toward molecularly dissolved substances, and consequently it would seem unlikely that after the formation of the first ring a second and third ring could be formed. The view is put forward that true semipermeable media are solvated and when these become less solvated

holes appear through which the dissolved substance can diffuse and so go to form a second ring. J. F. S.

**Thermodynamical Theory of Explosions. I and II.** SIR J. B. HENDERSON and H. R. HASSÉ (*Proc. Roy. Soc.*, 1922, [*A*], **100**, 461—482).—A theoretical paper in which calculations are made of the maximum temperature and pressure of an explosion in a closed vessel, also the calculation of the curve of reversible adiabatic expansion of the products, and incidentally the ideal indicator diagram. The calculations are applied to a gun, in which the variation with time of the volume of the chamber, of the composition of the products, and the temperature and pressure of explosion are worked out and the value of the maximum pressure determined. The maximum temperature obtained with Mark I cordite is 3210°, and with *MD* cordite 2870°, whilst the maximum pressure of Mark I cordite is 8370 atmospheres or 55·1 tons/sq. in. J. F. S.

**Equation for the Velocity of Reaction of Hydrogen Peroxide and Potassium Permanganate.** JAN ZAWIDZKI (*Roczniki Chemji*, 1921, **1**, 135—139).—From the measurements of Baeyer and Villiger (A., 1900, ii, 719) on the course of the reaction between hydrogen peroxide and potassium permanganate, the author calculates that the time law of this reaction is expressed by the differential equation $dx'/dt=k_2(1-x')/\sqrt{a}\sqrt{x'}$. The velocity coefficient $k'=k_2/\sqrt{a}$ is calculated for $-16°$ and $+15°$ and the values 0·119 and 0·379 respectively are obtained. From these, the temperature coefficient of the velocity constant is found to be 1·452. J. F. S.

**The Velocity of Reaction in Mixed Solvents. II. The Velocity of Saponification of the Ethyl Esters of some Monosubstituted Benzoic Acids.** ALBERT ERIC CASHMORE, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1922, **121**, 243—253).

**Influence of Temperature on the Velocity of Interpenetration of Solids.** H. WEISS and P. HENRY (*Compt. rend.*, 1922, **174**, 292—294; cf. A., 1920, ii, 545; 1921, ii, 551).—From a study of the velocity of solution of silver antimonide, $Ag_3Sb$, in solid silver at different temperatures in the case of a silver–antimony alloy containing 14% of antimony, it is shown that the velocity is proportional to the temperature, being expressed by the equation $=Ka^T$, where $T$ is the absolute temperature and, in this case, $K=4{\cdot}17\times10^{-12}$, and $a=1{\cdot}0324$. W. G.

**The Mechanism of Catalytic Hydrogenation.** A. SKITA (*Ber.*, 1922, **55**, [*B*], 139—143).—In a recent communication, Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185) have pointed out the necessity of priming the platinum catalyst with oxygen during the course of hydrogenations and have advanced the hypothesis that a platinum peroxide or oxide is intermediately formed. This suggestion is quite consonant with the author's repeated observation that the activity of the catalyst produced in situ is

superior to that of the pre-formed agent, since the experimental conditions do not guarantee the complete absence of oxygen. Comparative experiments with a platinum catalyst produced in situ do not show any difference in the rate of hydrogenation of pulegone or *as-p*-xylidine when every trace of oxygen is excluded and when special precautions to this end are not observed; the formation of a peroxide as catalyst cannot therefore be assumed in these cases. Further, if the platinum catalyst is in reality a peroxide, its oxygen must liberate iodine from potassium iodide, and hydrogenation must be impossible in the presence of the salt. It is found, however, that phenol is reduced smoothly to *cyclo*hexanol at 40° in the presence of potassium iodide. On the other hand, the addition of potassium iodide completely inhibits the reduction of phenol or *as-p*-xylenol at the atmospheric temperature, whereas in its absence they are transformed readily into *cyclo*hexanol and 1 : 4-*dimethyl*cyclo*hexan*-2-*ol*, b. p. 179°, respectively. Reduction occurs quantitatively but slowly if the mixtures are heated at 50°. At the higher temperature, it appears, therefore, impossible that hydrogenation should depend on the formation of a platinum peroxide. It has not yet been elucidated whether the failure of the action at the atmospheric temperature is due to the inactivation of a platinum peroxide or to poisoning of the catalyst. H. W.

**The Mechanism of Catalytic Action in the Hydrolysis of Fats.** E. BRINER and (MLLE) A. TRAMPLER (*Helv. Chim. Acta*, 1922, **5**, 18—20).—The product obtained by the sulphonation of phenylacetic acid is inferior to hydrochloric or sulphuric acid as a catalyst in the hydrolysis of ethyl acetate in homogeneous solution. It thus appears that the presence of a common group in catalyst and substrate does not confer any supplementary chemical activity on the former. In Twitchell's and similar catalysts, the activity of the sulphonic group is diminished by the presence of the aliphatic radicle, but this effect is more than compensated by the greater mutual solubility caused by the two similar groups. H. W.

**Conclusions from the Spherical Form of the Simplest Atom.** L. ZEHNDER (*Physikal. Z.*, 1922, **23**, 53—55).—A theoretical paper of a highly speculative character, in which, on the basis of a spherical primordial atom, an atomic ether, the atoms of which have a mass of about one-millionth that of hydrogen, elasticity, and gravitational forces, the author draws a number of conclusions respecting the atomic weight of helium, the structure of the carbon atom, and the subdivision of organic compounds into three classes, aliphatic, aromatic, and carbohydrates. J. F. S.

**A New Model of the Nucleus.** MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 454—473).—Previous speculations (cf. A., 1921, ii, 479) are extended by the consideration of *iso*hydrogen particles, of mass 1. The disintegration series of thorium, uranium, and actinium are considered on the basis of this hypothesis. J. R. P.

**Structure of the Atomic Nucleus.** O. Chwolson (*Z. Physik*, 1921, 7, 268—284).—A theoretical paper in which an attempt is made to deduce the structure of the atomic nucleus. It is maintained that any hypothesis of the structure of the atomic nucleus must conform to the following: (1) the mass of the atomic nucleus is practically the same as that of the atom, (2) the positive charge, $E$, of the nucleus is $eN$, where $-e$ is the charge of the electron, and $N$ the atomic number of the corresponding element, (3) the atomic weight is roughly $M=2N$, (4) in the case of hydrogen $M=2N$ is not true, and (5) the hypothesis must not be in conflict with Bohr's hypothesis. As the basis of the present hypothesis, the author assumes that the volume density, $\delta$, of electricity of both signs is a constant and that a given charge, $E$, irrespective of its sign, has the same volume, $v=\delta/E$. From this it is shown that the atomic nucleus cannot easily he represented as a sphere built up of spherical particles, and the assumption is made that it is cylindrical and is built up of disks. This conception is strictly in keeping with the relatively large volume of the nucleus in comparison with that of the electron. It is further assumed that the positive elementary disk is identical with the helium nucleus and the $\alpha$-particle. The elementary positive disk is termed the "pentalon." Negative electricity consists of spherical electrons and positive electricity of disk-shaped pentalons. If $-e$ is the charge of an electron, $e'$, the charge of the pentalon is $e'=2e$; the mass of the pentalon is $m'=4$. The order number of the pentalon $N'$ is $N'=N+1$, where $N$ is the atomic number of the element. The atomic nucleus is a disk or cylinder made up of pentalons, between each pair of which is a disk of negative electricity, of charge $-e$, equal to that of an electron. The disk of negative electricity is termed a "piezo-electron" and its order number is $N''=N-2$. The atomic nucleus of an element of atomic number $N$ consists of $N-1$ pentalons and $N-2$ piezo-electrons; these $2N-3$ disks form a cylinder which has no interstices. The charge of the nucleus is $E=(N-1)2e-(N-2)e=Ne$. Calculating from the above, it is shown that the radius of the pentalon is $69{\cdot}9s$, where $s$ is the radius of the electron, and the thickness, $D$, is $0{\cdot}0005450s$; the radius of the piezo-electron is also $69{\cdot}9s$, and the thickness is half that of the pentalon. The pentalon has a mass which is 7340 times that of the electron. The thickness $D(N)$ of the nucleus of an element of atomic number $N$ is $D(N)=(N-1)D+(N-2)D/2=(3N-4)D/2$ and the mass, $M_1=4(N-1)+2(N-2)=2N$. The hypothesis is compared with the Bohr hypothesis, and found not to conflict with it. The hydrogen nucleus on the basis of the hypothesis is shown to be built up of one pentalon and one piezo-electron, both of double thickness and of reduced radii in the ratio $1:\sqrt{2}$. That is, the hydrogen nucleus is three times as thick as the helium nucleus, and has a radius $49{\cdot}5s$ and a thickness $0{\cdot}001635s$. J. F. S.

**Attempt [to Find] a Physical Basis for Atomic Radiation.** E. Gehrcke (*Z. Physik*, 1921, 6, 400—402).—The author imagines

*the electrons surrounding an atomic nucleus as rings round the* nucleus and not as spheres rotating in an orbit round the nucleus. The ring form of the electron has the same mass, volume, and surface as the spherical electron, and is to be regarded as a spacial isotope of the spherical electron. If for any reason the ring electron changes its diameter, a change in the ether must also occur, and this change in the ether gives rise to emission or adsorption; emission when the ring reduces its diameter and absorption when the diameter increases. The change in the diameter of the ring consists in the displacement of the ether over the space between the initial and final positions of the ring. The mechanism of this *process is visualised as follows. An atomic ether, E, the atoms of* which are arranged in a space lattice, is assumed. The space lattice has spherical symmetry in the neighbourhood of a positive atomic nucleus. Between the atoms of $E$, a magnetic ether, $M$, is assumed, which in comparison with $E$ can be regarded as a continuum. The atomic ether, $E$, is the carrier of electric forces and is named the electric ether. The magnetic ether can spread out in stream lines (magnetic field lines), whilst the electric ether cannot spread out in the same way, but may change the shape of its space lattice. The sudden change of the space lattice, due to a change in diameter of the ring electron, occasions vibrations in the ether atoms which are transmitted to neighbouring ether atoms, and when the transmission of the vibration extends outside the ring emission of radiation results. Absorption results when incoming vibrations increase the kinetic energy of the ring electron, that is, increase its velocity and so increase its diameter. It is therefore not the ring electron which makes the spring at each energy step, but the $E$ ether which is displaced by the thickness of a ring electron. The generator of light and Röntgen radiation in the material atom is, therefore, not a vibrating electron, but the whole system of ether atoms between two radii, $R$ and $r$, swinging in a pendulum-like manner. The frequency, $\nu$, of the vibrations of the ether atoms is given by the ether between the radii $R$ and $r$, and is proportional to the thickness and inversely proportional to the square of the length, that is, $\nu \sim R-r/Rr=1/r-1/R$. J. F. S.

**Condition of Motion of Molecules in Space.** J. Böeseken, Chr. van Loon, Derx, and P. Hermans (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **24**, 198—204).—A theoretical paper in which it is shown that atoms which are not directly bound to one another exercise a mutual action on other atoms in the same molecule. Saturated non-cyclic molecules execute, among others, movements in which the parts of the molecule revolve in opposite directions, or with different velocities round the single bonds as axes. In the case of non-uniformly loaded molecules, that is, practically all molecules except those of hydrogen, nitrogen, oxygen, ethane, hexachloroethane, and similar molecules, the movements are irregular, because the most stable position of the atoms will be passed most frequently. In the saturated cyclic molecules with six or seven atoms, the ring-forming atoms are not fixed in one

plane, but lie in a curved surface which travels through space in undulatory movements; the atoms in this surface are under no tension. J. F. S.

**Transition Elements and the Octet Theory: A New Arrangement of the Rare Earth Elements in the Periodic Classification.** R. G. W. Norrish (*Chem. News*, 1922, **124**, 16—22).—A theoretical paper in which the author considers the fourth postulate of Langmuir's octet hypothesis from the point of view of valency and colour of the ions produced in solutions of salts of the metals. A new arrangement of the periodic system is drawn up, which has as its basis that the transition elements and the rare earth metals have a variable electronic structure as far as the outermost shell of electrons is concerned. It is shown that the elements which yield coloured kations can all be grouped together in a rectangle which extends from groups 4*A* to 1*B* and from series IV to VI. These elements are assumed to possess the variable electronic structure. The rare earth metals which give coloured kations are sharply cut off from those which give colourless kations by this rectangle. The existing data concerning the characteristic infra-red frequency, the latent heat of vaporisation, the compressibility, and the magnetic susceptibility are tabulated with the periodic arrangement, and it is shown that these properties maintain a more or less high value inside the rectangle but fall off sharply on either side of it. The elements inside the rectangle (excluding copper, silver, gold, and zirconium) are paramagnetic, whilst to the right of the rectangle all the elements except tin, which is feebly paramagnetic, are diamagnetic and those to the left of the rectangle are either feebly paramagnetic or diamagnetic. It appears that the magnetic susceptibility and colour are dependent on the presence of an incomplete subsidiary ring in the atom. J. F. S.

**Radii of the Alkali Metals and the Alkali Metal Ions.** Richard Lorenz (*Z. Physik*, 1921, **6**, 271—275).—A theoretical paper in which the author has discussed the values previously obtained for the atomic radii (A., 1921, ii, 191) and the space filling of the atoms concerned. A new table of the atomic radii, ionic radii, and the space filling of the alkali metals and alkali metal ions has heen drawn up which is based on the present discussion and recent work of other investigators. J. F. S.

**A Lecture Experiment for Demonstrating the Dependence of the Antiseptic Action of Mercury Compounds on the Degree of Ionisation.** G. Joachimoglu (*Biochem. Z.*, 1921, **121**, 259—261).—The fermentation of dextrose by yeast with the visible production of carbon dioxide in fermentation tubes affords a means of demonstrating the antiseptic influence of mercuric ions. Addition of mercuric chloride inhibits fermentation completely, but repression of the ionisation by addition of sodium chloride gives a moderate evolution of carbon dioxide. Mercuric cyanide has practically no inhibiting influence. H. K.

# Inorganic Chemistry.

**The Steric Formula of the Molecule of Water.** JEAN PICCARD (*Helv. Chim. Acta*, 1922, **5**, 72—74).—It is only possible to explain certain physical properties of water if it is assumed that the centre of gravity of the positive charges of the molecule does not coincide with that of the negative charges. This asymmetry of the charges might result from the inequality in the distances of the two hydrogen atoms from the oxygen atom or by such a disposition of the hydrogen atoms that the valencies uniting them to the oxygen atom are disposed at an angle other than 180°. There is, however, no evidence in favour of the first supposition. A consideration of oxonium salts, on the other hand, shows that in them the co-ordinative valency of oxygen is three, and that the oxygen atom may be regarded as placed in the centre of an equilateral triangle with its valencies directed towards the apexes and therefore inclined to one another at an angle of 120°. An explanation is thus given for the observation that only those carbon–oxygen heterocyclic rings are stable in which the total number of atoms is five or six. Thus, for example, if the valencies of carbon form an angle of 109° 28′ witb one another and those of oxygen an angle of 120°, the mean deviation in a cyclic system composed of three carbon and three oxygen atoms is only 2° 38′ whereas in *cyclo*hexane the mean deviation is 5° 16′. H. W.

**Electrolytic Concentration of Aqueous Solutions of Nitric Acid. I.** HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1922, **193**, 89—95).—When a solution of nitric acid is electrolysed in a cell in which the anode and cathode are separated by a porous diaphragm, concentration of the acid occurs through electrolytic decomposition of water and at the same time the concentration of the acid in the anolyte is increased at the expense of that in the catholyte on account of the different migration velocities of the hydrogen and nitrate ions. The acid in the catholyte is further reduced by reduction to nitrogen oxides, hydroxylamine, or ammonia according to the nature of the cathode metal. Experiments were made in which 70—71% nitric acid was electrolysed in a diaphragm cell using platinum electrodes, and provision was made for returning the gaseous nitrogen oxides formed in the anolyte chamber back to the catholyte chamber. The current used was 6—8 amperes and the *E.M.F.* 3·0—6·5 volts. It was found possible thus to increase the concentration of aeid in the anolyte chamber to 99·65% $HNO_3$. The porous cylinder used underwent considerable disintegration in the process. [See further *J. Soc. Chem. Ind.*, 1922, 172A.]
E. H. R.

**Preparation of Silicic Acid and Tungsten Hydroxide Sols by means of Hildebrand Cells.** M. KRÖGER (*Kolloid Z.*, 1922, **30**, 16—18).—By the electrolysis of a 1·5% solution of sodium silicate

between a mercury cathode and a platinum anode in a Hildebrand cell sols of silicic acid are obtained which do not gelatinise until they have been kept for four weeks. A 6% solution gelatinises as soon as the solution becomes neutral. The electrolysis is started with a current of 0·55 ampere, but this steadily falls as the process proceeds, and in ninety minutes has reached the value 0·12 ampere. After one hundred and ten minutes' electrolysis, the solution has a neutral reaction toward litmus. In the case of the 6% solution, the gelatinisation proceeds so rapidly that the waves occasioned by stirring are often reproduced in the gel, which is usually as clear as glass. Electrolysis of a 30% solution of water glass causes silica to separate on the anode. Electrolysis of a 2% solution of sodium tungstate, using the apparatus named above with a silver anode, rapidly produces the hydrosol of tungsten hydroxide. The removal of alkali may be hastened by the cautious addition from time to time of a little hydrochloric acid, but in no circumstances may the neutral point be passed. Should the solution become acid, blue tungsten compounds are produced. The tungsten hydroxide hydrosols are clear and transparent, but of a deep brown colour, which in dilute solutions is yellowish-brown. They are coagulated by potassium chloride to form a black powder which resembles the lower oxides of tungsten. J. F. S.

**Influence of Tungstic Acid on the Gelatinisation of Silicic Acid in Concentrated Hydrochloric Acid Solutions.** M. Kröger (*Kolloid Z.*, 1922, **30**, 18—19).—The time required for the gelatinisation of silicic acid in the presence of tungstic acid by hydrochloric acid has been investigated. The solution consisted in each case of 7 c.c. of a solution of sodium silicate containing 33·7% of silica, to which had been added volumes of a 10% solution of sodium tungstate varying from 0·5 c.c. to 15 c.c., the total volume in each case being made up to 22 c.c. Nine c.c. of 9·77*N*-hydrochloric acid were added in each case and the time required for complete gelatinisation was noted. The time–tungstic acid concentration curve passes through a minimum at 1 c.c. of tungstic acid and a maximum at 2·5 c.c. of tungstic acid and then falls continuously. J. F. S.

**Frequency of the Electrons in the Neon Atom.** Laurence St. C. Broughall (*Phil. Mag.*, 1922, [vi], **43**, 339—344).—A mathematical paper in which the frequency, angular velocity, and linear velocity of the electrons in the neon atom have been calculated on the assumption that the electrons do not radiate energy under normal conditions. The following numerical results are recorded: Frequency of the electrons about the axis $XX'$, $n_3=0{\cdot}73\times10^{16}$; frequency about $YY'$ and $ZZ'$, $n'=1{\cdot}00\times10^{16}$; angular velocity about $XX'$, $\omega_3=4{\cdot}58\times10^{16}$ rad./sec.; angular velocity about $YY'$ and $ZZ'$, $\omega'=6{\cdot}28\times10^{16}$ rad./sec.; instantaneous linear velocity of the outer electrons about $XX'$, $v_3=2{\cdot}98\times10^{8}$ cm./sec.; instantaneous linear velocity of the outer electrons about $YY'$ and $ZZ'$, $v'=4{\cdot}08\times10^{8}$ cm./sec.; instantaneous linear velocity of the inner electrons about $YY'$ and $ZZ'=3{\cdot}83\times10^{8}$ cm./sec.

The value of $v$ is small when compared with the velocity of light, in consequence of which it follows that no appreciable error is committed in not correcting for the variation of mass with velocity according to the equation $m_v = m_0(1 - v^2/c^2)^{1/2}$, where $c$ is the velocity of light. J. F. S.

**Crystal Structures of the Alkali Haloids. I.** RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1921, **11**, 429—434).—From data as to the crystalline structure of the alkali haloids obtained from powder photographs and on the assumption that the unit cell consists of four molecules, it is held by the author that there are only two possible arrangements of the molecules within the unit cell, namely, the sodium chloride arrangement and the zinc sulphide arrangement. The geometrical considerations involved and the method of calculating the nature of the diffraction effects to be expected are given elsewhere (Wyckoff and Posnjak, following abstract). A closer accord of the normal decline of intensity of reflection with the spacing of the reflecting planes as observed in experiments on sodium chloride and similar crystals is obtained by assuming the intensity to be proportional to the 2·35 power of the spacing instead of the simple square. Experimental determinations of the intensity for a few of the principal lines of the spectrum were compared with the intensities calculated with alternative assumption of the two groupings above mentioned. The results agreed with the assumption of the sodium chloride grouping in the case of sodium bromide, sodium iodide, potassium bromide, potassium iodide, and rubidium chloride. Cæsium bromide and cæsium iodide have a similar structure to cæsium chloride, which has been shown to be body-centred (Davey and Wick, *Physical Rev.*, 1921, **17**, 403). G. W. R.

**Crystal Structure of Ammonium Platinichloride.** RALPH W. G. WYCKOFF and EUGEN POSNJAK (*J. Amer. Chem. Soc.*, 1921, **30**, 2292—2309).—The crystal structure of ammonium platinichloride has been determined by a general method which is based on the theory of space groups. It is shown that crystals of ammonium platinichloride have a structure which is analogous to that commonly assumed for fluorspar, in which the $PtCl_6$ groups occupy the positions of the calcium in fluorspar or crystals and the $NH_4$ groups the positions of the fluorine. The unit crystal cell has a side $9{\cdot}843 \times 10^{-8}$ cm. The only assumption made which is not required in the ordinary determination of the wave-length of $X$-rays from a reflection spectrum is that the four hydrogen atoms of the ammonium radicle are exactly alike, with this exception, that in attempting to place the chlorine atoms with accuracy, it was assumed that atoms scatter $X$-rays in an amount which is roughly proportional to their atomic numbers and that in a lattice arrangement of atoms the intensities of reflection follow quantitatively the order of $1/(h^2+k^2+l^2)$. J. F. S.

**Revision of the Atomic Weight of Glucinum. Analysis of Glucinum Chloride.** O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1922, **55**, [*B*], 4—12).—The ratios $BeCl_2 : 2Ag$ and

$BeCl_2$ : 2AgCl have been determined in the same manner as used previously in the determination of the atomic weight of bismuth (Hönigschmid and Birckenbach, A., 1921, ii, 646). As mean result of all analyses, the value Gl=9·018 is adopted, this figure being about 1% lower than that assigned by the International Commission.

Technical glucinum carbonate is converted into the basic acetate and purified from iron compounds by repeated crystallisation from glacial acetic acid. The purified acetate is sublimed and converted into the nitrate. The solution of the latter in water is treated with an excess of ammonium carbonate and filtered from any undissolved aluminium compounds; the glucinum carbonate is subsequently precipitated by boiling the filtrate, and is finally converted into the oxide by calcination in a platinum dish in an electrically heated furnace. The pure oxide is transformed into the chloride by ignition with carbon in a current of chlorine. The apparatus used is identical with that described previously (*loc. cit.*). Great caution is needed in the quantitative decomposition of glucinum chloride by water.

Glucinum chloride has $d_4^{25}$ 1·8995. H. W.

**Inorganic Luminescence Phenomena. IV. Preparation of Pure Magnesium Sulphide and its Phosphorescence. II. Phosphorescent Magnesium Sulphides.** ERICH TIEDE and FRIEDRICH RICHTER (*Ber.*, 1922, **55**, [*B*], 69—74).—The specimens of magnesium sulphide described previously (A., 1916, i, 619) were not sufficiently pure to allow definite conclusions to be drawn with respect to the capacity of the substance to phosphoresce. Pure magnesium sulphide has now been prepared by the ignition of magnesium oxide or, preferably, of anhydrous magnesium sulphate in a current of nitrogen laden with carbon disulphide vapour. The compound is not phosphorescent, but becomes so by suitable additions of manganese, bismuth, or antimony, the optimal amount of metal for 1 gram of sulphide being 0·001—0·002 gram of manganese as sulphate or chloride, 0·0024 gram of bismuth as the basic nitrate, and 0·0013 gram of antimony as potassium antimonyl tartrate. The main band of emission of phosphorescent light in the case of magnesium sulphide containing manganese lies in the red, approximately between 615 and 765 $\mu\mu$ with a maximum at 720 $\mu\mu$. The intensity at the atmospheric temperature for metal content from 0·00023—0·004 gram is almost constant and not markedly dependent on wide variations of temperature and duration of ignition. The duration of the phosphorescence is small. Magnesium sulphide containing bismuth exhibits an intensely blue phosphorescence which is excited by daylight or arc or mercury-vapour light. The band lies between 430 and 550 $\mu\mu$ with a maximum at 465 $\mu\mu$. Specimens of magnesium sulphide containing antimony have a delicate, yellow colour and a persistent, intensely yellowish-green phosphorescence after excitation by daylight or arc or mercury-vapour light, or, particularly, by exposure to cathode rays. The band lies between 570 and 610 $\mu\mu$ with a maximum at 545 $\mu\mu$. H. W.

**Lead in the Uranium Minerals of Madagascar.** MUGUE (*Compt. rend.*, 1922, **174**, 172—173).—The industrial treatment of several tons of betafite from Madagascar resulted in the isolatic of lead to the extent of 0·6% of the mineral treated. The minera being perfectly crystalline and practically free from impurities, th lead apparently occurs in the same chemical form as the uraniur and is a disintegration product of uranium. The radioactivity of this lead has increased regularly for six months. W. G.

**Abnormal Crystallisation of Lead Azide by Protectiv Colloids.** A. G. LOWNDES (*Trans. Faraday Soc.*, 1921, 16 Appendix, 128—129).—Lead azide when formed in large crysta is liable to explode and is therefore not entirely suitable fo detonators. It is generally held that the explosions are caused b the fracture of large crystals. It is shown in preparing lead azid that if instead of running sodium azide and lead acetate solution into water the solutions are run into a 0·5% solution of gelatin o dextrin small crystals which are not liable to fracture are pro duced. The presence of ferric chloride also causes the formatio of small crystals, bnt these are useless for the filling of detonators A number of photomicrographs of lead azide prepared by th various methods are included in the paper. J. F. S.

**Preparation of Catalytic Copper.** JEAN PICCARD (*Helv Chim. Acta*, 1922, **5**, 147—148).—The following modified metho (cf. Piccard and Larsen, A., 1917, i, 644) yields catalytic coppe which is superior in its activity to Kahlbaum's "copper-bronze" or "naturkupfer C."

Granulated zinc (600 grams) is mixed with finely-powdere potassium dichromate (190 grams) or, preferably, with an equa weight of hydrated sodium dichromate, in a three-litre flask an concentrated hydrochloric acid (1300 c.c.) is added within fiv to ten minutes. A vigorous action ensues which leads to the forma tion of a clear, blue solution. The latter is filtered through glas wool into a flask filled with carbon dioxide, a current of the ga heing passed over the filter during the process. The solution is treated with brisk agitation with copper sulphate (120 grams dissolved in ice-cold water (700 c.c.). Reduction is instantaneous The precipitated copper is washed five times by decantation with water, then filtered, and washed successively with ordinary and absolute alcohol and benzene. If the product is to be dried, the final washing should be effected with benzene containing a little vaselin. After desiccation in a vacuum, the copper is relatively stable towards air, but is preferably preserved in evacuated sealed tubes. It may also be stored as a paste beneath alcohol. H. W.

**Colloidal Copper Hydroxide.** C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 1—5).—The preparation of solid colloidal copper hydroxide is described. To 50 c.c. of 2% sodium prot- albinate solution, which acts as protective colloid, 20 c.c. of *N* sodium hydroxide and 20 c.c. of 1% copper sulphate solution are added alternately in small quantities at a time. A light blue

turbid sol is produced which is dialysed for four days, treated with 3 drops of *N*-sodium hydroxide, and evaporated to dryness at 60° in a vacuum. A blackish-blue, brittle substance is obtained in the form of lamellæ which dissolve in water to form the original sol. The solid colloid contains 14·02% of copper and 1·34% of sodium. By using sodium lysalbinate as protective colloid and varying the quantities of the other reagents, solid colloids, similar in appearance and properties to the above but varying in composition, may be obtained. The colloid richest in copper contains 35·47% of copper and 5·31% of sodium. If solutions of the sols are heated for some time on a water-bath black lamellæ are deposited which dissolve in water to give a dark brown, turbid hydrosol. This does not change in colour when treated with 4*N*-ammonia solution, even after keeping for four days. The product is regarded as colloidal cupric oxide, and has been obtained containing 28·58% of copper and 4·37% of sodium. J. F. S.

**The Peroxidic Compounds of Copper.** (MISS) JOAN ALDRIDGE and MALCOLM PERCIVAL APPLEBEY (T., 1922, **121**, 238—243).

**Reduction of Solutions of Ferric Salts with Mercury.** LEROY W. MCCAY and WILLIAM T. ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 2372—2378).—Neutral and acid solutions of ferric chloride are completely and rapidly reduced when shaken with a little mercury. In the case of ferric sulphate, the reduction proceeds to an equilibrium which at 20° lies at about 53% of ferrous iron, but if a little free hydrochloric acid or sodium chloride is added the reduction becomes complete. Under similar conditions, solutions of titanic acid are not reduced. If the mercurous salt is filtered off, the ferrous iron in the solution may be estimated by titration with either potassium permanganate or dichromate. Experiments on the estimation of iron in ferric alum and other ferric compounds show that this constitutes a rapid, accurate, and convenient method. Solutions of potassium ferricyanide, potassium chromate, ammonium molybdate, sodium vanadate, and potassium antimonate when acidified with hydrochloric acid are all reduced when shaken with mercury. J. F. S.

**Strengths of Cobaltammine Bases and Werner's Theory of Bases.** ARTHUR B. LAMB and VICTOR YNGVE (*J. Amer. Chem. Soc.*, 1921, **43**, 2352—2366).—The relative strengths of the following cobaltammine bases: hexamminecobaltic dibromide dihydroxide, hexamminecobaltic hydroxide, aquopentamminecobaltic hydroxide. diaquotetramminecobaltic hydroxide, triethylenediaminecobaltic hydroxide, diaquodiethylenediaminecobaltic hydroxide, carbonatotetramminecobaltic hydroxide, 1 : 2-dinitrotetramminecobaltic hydroxide, 1 : 6-dinitrotetramminecobaltic hydroxide, and dinitroaquotriamminecobaltic hydroxide have been determined by measuring the electrical conductivity over a range of concentrations at 25° and comparing these with the conductivities at zero concentration, as calculated from conductivity measurements of salts derived

from these bases. The determinations show that these bases are very strong, some of them being as highly ionised as potassium hydroxide; the replacement of ammonia by ethylenediamine has no effect on the strength of the base. The replacement of ammonia by water molecules produces a marked and progressive decrease in the strength; the substitution of acid-groups has no marked effect on the strength, the electrostatic effect of a decrease in valency probably counteracting the chemical effect of the acid radicle; the stronger acid radicle produces the weaker base. There is no marked difference in the ionisation of the successive hydroxyl groups in hexamminecobalt hydroxide. The improbability of the distinctive features of Werner's theory of bases is pointed out, and a more probable interpretation suggested. Equations have been derived, giving an important correction of the conductivity of solutions of bases for the conductivity of the carbon dioxide dissolved in the water. These equations have been applied in the present work. J. F. S.

**Sub-salts of Bismuth.** HENRY GEORGE DENHAM (*J. Amer. Chem. Soc.*, 1921, **43**, 2367—2371).—Making use of the method and apparatus formerly employed in the preparation of the sub-salts of lead (T., 1917, **111**, 29; 1918, **113**, 249; 1919, **115**, 109), the author has prepared sub-salts of bismuth from bismuth sub-oxide. The products obtained are a sub-oxyiodide, $2BiI_2,3BiO$, the sub-iodide, $BiI_2$, and bismuth dimethyl. The *sub-oxyiodide* is a non-volatile, brick-red substance which is stable in dry air; it commences to decompose at 350°. A saturated solution gives a faint darkening with hydrogen sulphide and a faint turbidity with silver nitrate. It is decomposed into the metal and a soluble tervalent bismuth salt by sulphuric, hydrochloric, and acetic acids. It is insoluble in alcohol and in aqueous potassium iodide solutions and reduces acid solutions of potassium permanganate. *Bismuth sub-iodide* is a volatile substance which crystallises in red, orthorhombic needles. In aqueous solution, it gives stronger reactions for bismuth and iodine than the oxyiodide; it dissolves freely in potassium iodide solution, giving solutions of the colour of dichromate solutions. It speedily reduces aqueous solutions of iodine and acid permanganate, and is decomposed at 400° into bismuth tri-iodide and metallic bismuth. The distillate of excess methyl iodide from the preparation of the above compounds was yellow in colour, but on exposure to air it became colourless, and a white solid which turned yellow on keeping separated. This white compound is probably *bismuth dimethyl*, and is insoluble in alcohol; it is a strong reducing agent, and on oxidation is converted into *bismuth dimethoxide*, $Bi(OCH_3)_2$. J. F. S.

# Mineralogical Chemistry.

**Chemical Aspects of Volcanism with a Collection of the Analyses of Volcanic Gases.** E. T. ALLEN (*J. Franklin Inst.*, 1922, **193**, 29—80).—The author has collected and tabulated all published analyses of volcanic gases of any importance for the purpose primarily of determining whether any relation exists between the composition of the gases and the temperature at which they issue from the ground. The analyses are made the basis of a critical inquiry into the nature of the original gases and into the extent to which they have become contaminated with atmospheric gases and water. Consideration of the gases contained in igneous rocks leads to the conclusion that these are the source of the original volcanic gases, of which the most important is water. The original gases are probably changed in composition by the time they reach the point of collection; in some cases they probably lose a portion of the strong acid gases by interaction of these with metallic oxides; in most cases they become diluted with steam from surface waters and by atmospheric gases. In some volcanic gases the relations between the inert gases, argon and nitrogen, point to an atmospheric origin for these constituents; in others, they must either be of deep-seated origin or their original atmospheric relation has been changed by selective solubility in the magma. The composition of the original gases may also be changed by interaction with mineral substances, by surface oxidation, or by the shifting of chemical equilibrium due to change of temperature. Such equilibria as the following may be affected: $CO_2+H_2 \rightleftharpoons H_2O+CO$; $3S_2+4H_2O \rightleftharpoons 4H_2S+2SO_2$; $H_2S+2H_2O \rightleftharpoons 3H_2+SO_2$; $2H_2S \rightleftharpoons 2H_2+S$. These and other reactions are discussed from the thermal point of view. A more or less abrupt evolution of gas from the magma may occur during crystallisation. Energy derived from shifting chemical equilibria may have a considerable influence in prolonging the life of an eruption, but not in initiating volcanic activity. Surface combustion is sometimes an important factor in keeping up the temperature. Secondary explosions of great violence are undoubtedly produced by the access of surface water to hot volcanic ejecta. Primary explosions are probably the result of pressure from magmatic gases, not the result of chemical action. E. H. R.

**Absence of Cobalt in Cornetite.** ALFRED SCHOEP (*Min. Mag.*, 1922, **19**, 301—302).—Cornetite from the original locality, Star of the Congo mine in Katanga, Belgian Congo (A., 1920, ii, 441), is intimately mixed with minute black specks of heterogenite (A., 1921, ii, 649). When freed from these, the mineral shows no cobalt when tested microchemically with mercury thiocyanate. It thus agrees completely with the cornetite from Bwana Mkubwa in Northern Rhodesia (A., 1921, ii, 701). L. J. S.

**Chemical Investigation of Japanese Minerals containing Rarer Elements. II. Analysis of Columbite and Monazite of Ishikawa, Iwaki Province.** YÛJI SHIBATA and KENJIRÔ KIMURA (*J. Chem. Soc. Japan*, 1921, **42**, 957—964; cf. A., 1921, ii, 269).—Columbite (*d* 5·59) from Ishikawa, Iwaki Province, gave on analysis:

| $Nb_2O_5,Ta_2O_5$. | $SnO_2$. | $Al_2O_3$. | MnO. | FeO. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|
| 78·94 | 0·38 | 0·36 | 3·56 | 15·99 | 0·90 | 100·13 |

with traces of $SiO_2$, $TiO_2$, $WO_3$, and CaO. The amount of $Ta_2O_5$ was about 10%. The ratio (Fe,Mn)O : $(Nb,Ta)_2O_5$=1 : 1·03.

Monazite (*d* 5·17) from the same locality gave on analysis:

| $P_2O_5$. | $SiO_2$. | $UO_3$. | $ThO_2$. | $Al_2O_3$. | $Fe_2O_3$. | $Ce_2O_3$. | $(La,Nd)_2O_3$, etc. | $Y_2O_3$, etc. | CaO. | MgO. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 27·52 | 2·98 | 0·42 | 11·08 | 0·80 | 0·66 | 21·08 | 31·27 | 3·53 | 0·52 | 0·27 | 0·56 | 100·69 |

Various samples differed; some contained traces of $ZrO_2$, $TiO_2$, and $SnO_2$, whilst others did not contain $UO_3$, and the quantities of $ThO_2$ and $SiO_2$ were very irregular. On spectroscopic examination, lines of praseodymium, gadolinium, dysprosium, erbium, ytterbium, holmium, and terbium were observed. K. K.

**Density, Refractivity, and Composition Relations of some Natural Glasses.** C. E. TILLEY (*Min. Mag.*, 1922, **19**, 275—294).—The natural glasses fall into two groups: (*a*) tektites, including moldavites and australites, which are perhaps of meteoric origin, and (*b*) volcanic glasses, including rhyolitic, trachytic, and basaltic obsidians. The refractive index and density were determined for a number of these, and their specific refractivity ($r_G=(n-1)/d$) compared with that of artificial glasses of definite composition (silica, felspars, and $CaSiO_3$–$MgSiO_3$). When plotted on graphs, the different glasses fall in well-defined areas according to their composition. Values for the specific refractivity of various rock-constituents in a state of glass are calculated. An analysis is given of tachylyte forming the selvage of a basic andesite at Kildonan, Eigg, Western Isles of Scotland. An estimation of water in the pitchstone of Newry, Ireland, gave 7·04%. The presence of water has a marked influence on the specific refractivity, as shown in the case of analysed rhyolite-obsidians from the Island of Lipari. L. J. S.

**Augite from Hawaii.** HENRY S. WASHINGTON and H. E. MERWIN (*Amer. J. Sci.*, 1922, [v], **3**, 117—122).—Loose, jet-black crystals of augite from the volcano of Haleakala on the island of Maui, were powdered and pure material separated by heavy solutions and the electromagnet, *d* 3·358. In thin sections the material is pale grey with a darker surface film; extinction-angle 47° (red) to 49° (blue), α 1·700, β 1·706, γ 1·724. An analysis of the powder aied at 110° gave:

soa.
adde

| $TiO_2$. | $Al_2O_3$. | $Cr_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ·89 | 6·82 | 0·23 | 3·36 | 4·43 | 0·16 | 21·35 | 13·34 | 0·65 | 0·03 | 0·15 | 100·11 |

Tschermak's (A., 1921, ii, 121), Boeke's (A., 1914, ii, 283), and Zambonini's (1914) views as to the constitution of aluminous augites are criticised; and the alumina and excess of ferric oxide are regarded as being in solid solution in the pyroxene constituents (diopside-hedenbergite, acmite-jadeite, and clinoenstatite). The present analysis is interpreted as $CaMgSi_2O_6$, 69·12; $CaFeSi_2O_6$, 15·13; $NaFeSi_2O_6$, 5·08; $MgSiO_3$, 1·90; $FeSiO_3$, 0·40; $(Al,Fe)_2O_3$, 8·65%. Assuming, with Zambonini, that the alumina is present as spinel (12·23%), there remains a residue of silica (4·20%) and $CaSiO_3$ (6·61%). L. J. S.

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# Analytical Chemistry.

**A Microvolumenometer.** A. Bolland (*Roczniki Chemji*, 1921, **1**, 147—156).—A volumenometer is described which consists of a thick-walled capillary tube which is closed at its lower end; the tube is 50 mm. long and has a capacity of 0·02 c.c., it is accurately graduated into forty divisions each corresponding with 0·0005 c.c. and widens at the top into the shape of a test-tube 40 mm. long. The method of weighing, filling, and emptying the apparatus is described. It is shown that it may be used for quantitative micro-analysis by measuring the volume of precipitates after centrifuging. J. F. S.

**Standard Dropping Pipette.** Hede Halphen (*Pharm. Zentr.-h.*, 1921, **62**, 767—768).—A pipette which will deliver 20 drops of water per gram should have an orifice 3 mm. in diameter (external measurement); such a pipette can be made by drawing out a glass tube at one end and passing this narrow portion as far as it will go through a 3 mm. hole drilled in a brass plate. The tube is then cut exactly at the surface of the plate. W. P. S.

**Rapid Extraction Funnel.** H. Wolffram (*Chem. Ztg.*, 1922, **46**, 93).—A very simple apparatus to replace a Soxhlet extractor consists of a cylindrical part somewhat wider than the extraction thimble to be employed, narrowing below to an outlet tube in the usual way. A small glass triangle prevents the thimble from closing up the way into the outlet tube, and three or four indentations in the sides of the glass cylinder prevent the thimble from leaning over against the side of the glass. G. F. M.

**Proposed Standard Method of Colorimetry.** Herbert E. Ives (*J. Opt. Soc. Amer.*, 1921, **5**, 469—478).—For the purpose of simplifying spectrometric measurements for colour specification, the author has designed a method of colour measurement, which consists essentially of the spectrophotometry of adjacent patches of the spectrum, each patch of a width fixed by the hue scale, and

narrow enough so that there is no colour difference in the spectrophotometer field at each setting. The number of patches is determined by the kind of colour and the degree of accuracy required. An instrument is described by which the measurements can be made and in which any colour may be reproduced for comparison.

J. F. S.

**The Salt Error of Coloured Indicators.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 54—67; cf. Sørensen, A., 1909, i, 861; 1910, i, 147).—The corrections that should be made for the presence of solutions of sodium chloride and potassium chloride of concentrations ranging from decinormal to normal have been determined for a large number of indicators. The results are discussed in detail for each indicator and a table summarising the chief results is appended, together with notes as to the suitability of the different indicators for various conditions. H. J. E.

**The Colorimetric Estimation of Hydrogen-ion Concentration without Buffer Solutions.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 104—118).—Hydrogen-ion concentration may be estimated by comparing the colour given with standard indicators with the colours given by mixtures of coloured salts in specified proportions. For many indicators, suitable comparison solutions may be made by mixing a solution of 11·262 grams $FeCl_3,6H_2O$ in 250 c.c. of 1% hydrochloric acid solution with a solution of 18·2 grams of crystallised cobalt nitrate in 250 c.c. of 1% hydrochloric acid solution; both these solutions may be employed after long keeping. Mixtures of these salt solutions in various proportions given in the tables show the same tints as the following: Neutral-red in solutions with range $p_H$ from 7·0 to 8·0; methyl-orange, range 3·05—4·60; tropæolin-*OO*, range 1·80—3·00; methyl-red 5·2—6·0. For solutions having $p_H$ between 4·2 and 6·0, where methyl-red is used as indicator, suitable comparison solutions may be made up with permanganate solution (0·004*N*) and dichromate solution (0·01*N*—potassium dichromate in 0·4*N*—$H_2SO_4$), but these solutions are not stable in colour, and must be prepared afresh as required. For the range 4·4—6·0 with this indicator, the ferric chloride solution may be mixed with one obtained by mixing 10 c.c. of 0·025% pure methyl-red solution with 10 c.c. of 4*N*-acetic acid solution, and diluting to 250 c.c.; the latter solution is stable for about a week.

For the range of $p_H$ between 8·2 and 10·0, with phenolphthalein as indicator, the comparison solutions are best prepared by adding to 10 c.c. of 0·5*N*-sodium carbonate solution given volumes of a 0·004% phenolphthalein solution. From the figures prepared for this table, the dissociation constants of phenolphthalein have been calculated; the values agree approximately with the figures deduced from theory (assuming the indicator is a bibasic acid) by Rosenstein (A., 1912, ii, 893).

For the range of $p_H$ between 6·0 and 7·0, *p*-nitrophenol is a suitable indicator, the colour comparison solutions being prepared in this case also from an alkaline solution of the indicator. With this

nge completed, it is possible to use the method for all values of ı between 2·0 and 10·0. S. I. L.

**The Titration of Moderately Strong Acids or Bases in the resence of Very Weak Ones.** I. M. KOLTHOFF (*Pharm. Weekad*, 1922, **59**, 129—142).—The observation of Tizard and Boeree :., 1921, **119**, 132) that the hydrogen-ion concentration is equal ı $\sqrt{K_1K_2}$ in the case of two acids having the same concentration, the presence of sufficient alkali to neutralise the stronger one, ıd where $K_1$ and $K_2$ are the dissociation constants of the two ids, is confirmed theoretically and by experiment. To obtain curate results by titration, it is necessary that the ratio $K_1 : K_2$ ıould be not less than $1 \times 10^4$, and the approximate concentrations ust be determined before the final titration is made. For this ırpose, the approximate concentration of both acids is first termined by titration with *N*-sodium hydroxide solution in esence of tropæolin-*O*, and the concentration of the stronger id by titration in presence of neutral-red or phenol-red. The ılue of $p_H$ can then be calculated from the above, and a comırison solution made up from the sodium salt of the strong acid ıd the necessary proportion of the weak acid, or a buffer solution the same $p_H$ can be selected. With this comparison solution to ve the colour required for the particular indicator employed, e accurate titration may be made. Generally, neutral-red or ı indicator of the same transition range is most suitable. S. I. L.

**Formation of Nitrogen Oxides in the Slow Combustion ıd Explosion Methods in Gas Analysis.** G. W. JONES and . L. PARKER (*J. Ind. Eng. Chem.*, 1921, **13**, 1154—1155).—hen the time of burning is not more than three minutes and e platinum wire is not heated above bright yellow, the formation nitrogen oxides in the slow combustion method does not exceed )03 c.c., and nitrogen oxides are not produced in the explosion ethod when air is used as the oxygen supply. If a mixture of : and oxygen is employed in the explosion method, appreciable ıantities of nitrogen oxides are formed and the error thus introıced may amount to 2%; their formation is due to increase in e flame temperature produced by the addition of oxygen.
W. P. S.

**Estimation of Water in Fuels.** ANDRÉ MARINOT (*Ann. ıim. Analyt.*, 1922, [ii], **4**, 7—8).—In the estimation of water in fuels or fuel oils, errors may be introduced by the absorption of oxygen or the distillation of anthracene concurrently with the evaporation of the water, even at temperatures below 100°. These errors are avoided by carrying out the operation in a current of dry hydrogen, and an apparatus is described for the purpose consisting of two 100 c.c. flasks connected together and heated in a constant level water-bath. From 10—15 grams of the material are placed in each flask and a slow current of hydrogen dried in a calcium chloride–sulphuric acid tower is passed through for one and a half hours. The vapours from the flasks pass through a

horizontal elongated bulb where any anthracene is deposited into a weighed **U**-tube containing calcium chloride, the exit of which is protected from atmospheric moisture by a guard tube.

G. F. M.

**Potassium Ferricyanide as a Reagent in Iodometry.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 66—68).—The accuracy of the author's method of standardising thiosulphate solutions by the use of potassium ferricyanide (*ibid.*, 1919, **56**, 1618) having been questioned, a further examination has been made. The method is found extremely accurate and very rapid. The ferricyanide must be pure and dry, and if the zinc sulphate and hydrochloric acid used are free from iron, a perfectly white precipitate of zinc ferrocyanide is obtained, and the end-point with starch is very sharp. S. I. L.

**High Percentage Hydrogen Peroxide (Perhydrol) for the Estimation of the Total Sulphur in Illuminating Gas.** ALOYS KLEMMER (*Chem. Ztg.*, 1922, **46**, 79).—The sulphur compounds, including hydrogen sulphide, carbon oxysulphide, carbon disulphide, and mercaptan, are oxidised to sulphuric acid by passing the gas through a strongly alkaline solution of hydrogen peroxide. Ten c.c. of perhydrol are mixed with 80 c.c. of fairly concentrated sodium hydroxide, and the gas is led through the thick, crystalline paste consisting of sodium peroxide, $Na_2O_2,8H_2O$, which is formed, at a rate not exceeding 100 litres per hour. At the end of the operation the liquid is acidified with hydrochloric acid, boiled to expel the excess of hydrogen peroxide, and the sulphuric acid precipitated as barium sulphate. G. F. M.

**Estimation of Sulphur in Cast Irons and Steels.** ANDRÉ MARINOT (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 5—6).—Five grams of the metal are treated with a reagent consisting of 30 c.c. of 50% sulphuric acid and 60 c.c. of hydrochloric acid in an apparatus consisting of a conical reaction flask of 375 c.c. capacity surmounted by a vertical condenser into the top of which is ground a small pear-shaped gas washer from which a delivery tube leads into a flask containing 200 c.c. of a 2·5% solution of zinc acetate acidified with acetic acid. The gas washer consists of a vertical narrow tube surmounting the condenser and extending almost to touch the apex of a conical muff which surrounds it and is sealed to the tube at the base, where, however, it is perforated with five or six small holes which allow of the escape of the gas into the outer envelope of the pear and thence through the delivery tube into the zinc acetate flask. All the sulphur in the metal is evolved as hydrogen sulphide, and a slow stream of carbon dioxide is passed through the whole apparatus to displace the gas and prevent the formation of colloidal sulphur or organic sulphur compounds. The sulphur is finally estimated by oxidising the zinc sulphide formed in the flask by standard iodine solution and titrating back the excess. G. F. M.

**Estimation of Available Sulphur in Golden Sulphide of ntimony.** B. D. W. LUFF and B. D. PORRITT (*J. Soc. Chem. nd.*, 1921, **40**, 275—278T).—It is suggested that the "available ulphur" be estimated by extraction with carbon disulphide after he pigment has been heated at 150° for five hours in an atmosphere endered slightly alkaline with ammonia; this heating converts ny amorphous sulphur which may be present into a form which s soluble in the solvent. The carbon disulphide used should be urified previously by distillation over sulphur. W. P. S.

**Sulphates in Blood.** W. DENIS (*J. Biol. Chem.*, 1921, **49**, 11—317).—A nephelometric method for the estimation of inrganic sulphates in blood or plasma is described. Proteins are emoved by means of mercuric chloride and the precipitate proluced by the addition of acidified barium chloride solution is comared with a standard in a nephelometer. No evidence was btained of the existence in deproteinised blood of other compounds f sulphur. E. S.

**A Micro-method for Estimation of Nitrogen.** D. ACÉL *Biochem. Z.*, 1921, **121**, 120—124).—After destruction of the organic natter with sulphuric acid in the usual manner, the ammonia ormed is not distilled off, but is determined colorimetrically by Nessler's reagent. The control is treated with standard ammonium hloride solution until the colours match. The method is suitable or the estimation of nitrogen in as little as 0·001—0·003 c.c. of erum or urine if diluted for measurement. H. K.

**A Rapid Method for the Estimation of Ammoniacal Nitrogen.** R. MEURICE (*Ann. Chim. Analyt.*, 1922, [ii], **4**, —10).—In the estimation of ammonium salts by converting hem into hexamethylenetetramine and titrating the free acid hus produced, errors are likely to occur if phenolphthalein is used s indicator in the preliminary exact neutralisation of the amnonium salt owing to the uncertainty of this indicator in presence f ammonia. This error is eliminated if rosolic acid is used as ndicator for the preliminary neutralisation, but as under ordinary onditions it is also sensitive to hexamethylenetetramine a special levice is adopted to render it insensitive. After the mixture of mmonium salt and formaldehyde has been kept about thirty ninutes, an equal volume of ether is added, and the whole is well haken, whereby the rosolic acid passes into the ether and becomes nsensitive to the amine, although still sensitive to a strong base uch as sodium hydroxide. Titration of the free acid with standard lkali can now therefore be proceeded with until the appearance f a pale rose colour which persists on agitating the liquid with he ether. G. F. M.

**Precipitation of Arsenic Sulphide from Arsenates.** J. H. REEDY (*J. Amer. Chem. Soc.*, 1921, **43**, 2419).—The time required or precipitation of arsenic sulphide from solutions of arsenates nay be greatly reduced by the addition of a small quantity of a oluble iodide, such as ammonium iodide. The hastening of the

precipitation is due to the reduction of the arsenic acid to arsenious acid, according to the equations $H_3AsO_4+2HI \longrightarrow H_3AsO_3+H_2O+I_2$; $H_2S+I_2 \rightleftarrows 2HI+S$. The reaction is applied by adding 1—2 c.c. of *N*-ammonium iodide solution to the hot solution which contains 4 c.c. of 6*N*-hydrochloric acid in 40 c.c. of solution, just before the hydrogen sulphide is passed in. Precipitation begins immediately and is usually complete in four to five minutes. Complications arise in the precipitation of mercury and copper as iodides and in the partial reduction of mercury to the mercurous condition. This difficulty is, however, removed during the digestion with yellow ammonium sulphide which oxidises both metals to the higher valency, precipitating them as mercuric and cupric sulphides. J. F. S.

**Method for the Estimation of Free and Combined Carbon Dioxide.** J. A. SHAW (*J. Ind. Eng. Chem.*, 1921, **13**, 1151—1152).—A definite quantity of the solution under examination (for example, mine water) is drawn into a cylindrical bulb which is fitted at the top and bottom with three-way taps; the tap at the top connects with a small funnel for the introduction of the sample and with a measuring burette, whilst the tap at the bottom connects with a smaller cylindrical bulb and with a mercury reservoir. At the commencement of the operation the whole apparatus is filled with mercury. Any gas liberated from the sample is passed over into the burette, the upper tap is then closed and the mercury reservoir lowered so that the whole of the liquid is drawn into the lower cylinder, a low pressure being thus produced in the upper cylinder and above the surface of the liquid. The gas collecting in the upper cylinder is then forced over into the burette by raising the mercury reservoir, the tap between the two cylinders being meanwhile closed, and, by repeating these operations several times, the whole of the carbon dioxide may be collected and its volume measured in the burette. Concentrated sulphuric acid is added after the sample has been introduced into the cylinder when it is desired to estimate the total (free and combined) carbon dioxide. W. P. S.

**Laboratory Notes. [Estimation of Silica, Phosphorus in Iron, etc.].** ERNST MURMANN (*Österr. Chem. Zeit.*, 1921, **24**, 142).—In the estimation of silica, two evaporations with an intervening filtration are necessary in order to render the whole of the silica insoluble, care being taken that the evaporation is carried to complete dryness of the residue. To estimate phosphorus in iron, soil extracts, etc., the sample is evaporated with hydrochloric and nitric acid, and the residue heated in order to destroy any organic matter; by extracting the residue with nitric acid, the phosphoric acid is obtained in solution and it is not necessary to dissolve the ferric oxide resulting from the decomposition of the ferric nitrate during the heating. The grinding of ores is facilitated if the powder is moistened with ether, and graphitic carbon burns readily if it has been moistened previously with a small quantity of magnesium acetate solution. The use of chalk, mineral phos-

›hate, or bone-ash is recommended in place of sand in sand-baths, ›ince sand is liable to scratch glass vessels and cause them to break ›hen heated. W. P. S.

**Volumetric Estimation of Potassium.** MACHELEIDT (*Woch. Brau.*, 1922, **39**, 23—24).—A standard solution of sodium hydrogen ›artrate is prepared by dissolving 60 grams of tartaric acid and 6 grams of sodium hydroxide in water and diluting to 1 litre. Six grams of potassium hydrogen tartrate are added and the ›olution is shaken for several hours. Thirty c.c. are filtered off ›nd titrated with *N*/10-barium hydroxide solution. A second ›0 c.c. are shaken for one to two hours with 0·5—0·75 gram of ›he salt mixture to be tested, the solution is filtered into a tared ›asin and, without washing the filter, titrated with the barium ›ydroxide solution. The solution is weighed before and after ›ltering, and allowance is made for the loss. The difference ›etween the two titrations is calculated to potassium oxide. [See ›urther *J. Soc. Chem. Ind.*, 1922, 200.] A. R. P.

**Estimation of the Calcium Content of Blood.** R. WEISS ›*Deut. med. Woch.*, 1921, **47**, 1298; from *Physiol. Abstr.*, 1922, **6**, 68).—A small measured quantity of serum is placed in a specially ›raduated tube, ammonium oxalate is added, and the precipitate ›ashed on the centrifuge with water. It is dissolved in sulphuric ›cid and titrated with permanganate. The figures given are: ›ormal 12, in tetany as low as 4, in rickets as high as 18 mg. per ›00 c.c. E. S.

**Micro-estimation of Calcium in Whole Blood, Plasma, ›nd Serum by Direct Precipitation.** GUY W. CLARK (*J. Biol. ›hem.*, 1921, **49**, 487—517).—The method described is practically ›lentical with that of Halverson and Bergeim (A., 1916, ii, 270). E. S.

**Sensitiveness and Applicability of Qualitative Reactions. ›I. Strontium Ions.** O. LUTZ (*Z. anal. Chem.*, 1921, **60**, ›33—441; cf. A., 1921, ii, 596).—The minimum quantities of ›rontium which can be detected by various reagents are as follows: ›ı each case, 5 c.c. of the strontium salt solution were treated with ›5 c.c. of the reagent in the cold and the observation made after ›ve minutes. Sodium phosphate, 1 : 9400; sodium sulphite, › : 12000; ammonium oxalate, 1 : 50000; ammonium carbonate ›ıd ammonia (at 100°), 1 : 210000; sulphuric acid, 1 : 125000. ›he addition of 5 c.c. of alcohol increases the sensitiveness of the ›ılphuric acid test to 1 : 1400000. W. P. S.

**Estimation of Magnesium in Technical Nickel.** K. ›HALUPNY and K. BREISCH (*Chem. Ztg.*, 1922, **46**, 91).—For ›e estimation of small quantities of magnesium in technical nickel ›—15 grams of the metal must be used, and the filtration and ›ashing of the voluminous precipitate of nickel sulphide are very ›borious and a frequent source of error. The advantage of a

method whereby the magnesium could be precipitated whilst th nickel remained in solution is apparent, and the non-precipitatio of nickel phosphate from potassium nickelocyanide by sodiur phosphate affords a means of attaining this object. The analysi is carried out as follows: 15—20 grams of the metal are dissolve in nitric acid, and the solution is twice evaporated to dryness wit hydrochloric acid to precipitate silicic acid. To the filtered solutio is then added 5—10 grams of ammonium chloride, followed b bromine water and ammonia to precipitate iron, manganese, etc The filtrate is approximately neutralised with hydrochloric acid and a concentrated solution of potassium cyanide is added unti the precipitate of nickel cyanide is just redissolved, followed b 20 c.c. of 10% disodium hydrogen phosphate solution and a thir of the volume of concentrated ammonia. After keeping ove night, the crystalline precipitate of magnesium ammonium phos phate is separated, and washed free from nickel. It is dissolved i dilute hydrochloric acid and reprecipitated with sodium phosphat and ammonia (this step is necessary on account of the large exces of alkali cyanide, present during the first precipitation, whic causes somewhat too high results). The precipitate is collecte in a Gooch crucible, ignited, and weighed as magnesium pyrc phosphate in the usual way. G. F. M.

**Estimation of Zinc as Zinc Pyrophosphate.** D. BALAREF (*Z. anal. Chem.*, 1921, **60**, 442—448).—The precipitation of th zinc phosphate should be made under the following condition The slightly acid solution, containing ammonium chloride an ammonium phosphate is treated with ammonia until it is slightl alkaline in reaction towards litmus; the mixture is kept at th ordinary temperature for eighteen hours, then heated on a wate bath for fifteen minutes, and the precipitate is collected, ignitec and weighed. The amorphous precipitate which first forms whe zinc is precipitated as phosphate from a solution containin ammonium salts is not zinc phosphate but ammonium zinc phos phate; if the zinc is precipitated by treating the hot solutio with ammonia, ammonium zinc phosphate and zinc phosphate ar precipitated together, and the results obtained are too low (cf Austin, A., 1900, ii, 49, and Dakin, A., 1900, ii, 624). W. P. S.

**The Separation of Aluminium from Glucinum. III** HUBERT T. S. BRITTON (*Analyst*, 1922, **47**, 50—60; cf. A., 1921 ii, 657, 712).—Berzelius's method, consisting in boiling the pre cipitated hydroxides with ammonium chloride solution whereb the glucinum hydroxide is dissolved, is unsatisfactory, as no mean could be found by which the occlusion of glucinum hydroxide b aluminium hydroxide could be eliminated, the results being accord ingly low for glucinum and correspondingly high for aluminium Wünder and Wenger's sodium carbonate fusion method (A., 1912 ii, 687) is satisfactory, but the time required for an analysis i long, as two fusions are necessary for a complete separation. Th of iosulphate method in which the neutral salt solutions are boile

with an excess of sodium thiosulphate until evolution of sulphur dioxide has ceased does not give quantitative separations owing to adsorption of glucina by the aluminium hydroxide which is precipitated. Haven's ether-hydrochloric acid method (A., 1898, ii, 142) is quantitative and is one of the most satisfactory and easily manipulated of all the methods investigated. Of the remaining methods, none were investigated, but it is probable that only Kling and Gelin's basic acetate distillation method (A., 1914, ii, 867) and Renz's ethylamine method (A., 1903, ii, 729) are quantitative, and as the former requires considerable manipulation and time, and the latter involves the use of a large quantity of an expensive reagent, they have no particular feature to recommend them. G. F. M.

**Detection of Manganese with Benzidine and of Cobalt by means of the Thiocyanate Reaction.** HUGO DITZ (*Chem. Ztg.*, 1922, **46**, 121—122).—The author claims priority for the method described by Feigl and Stern (A., 1921, ii, 278) of detecting traces of manganese by the blue coloration produced on adding an acetic acid solution of benzidine to the peroxidised manganese compound formed by autoxidation in an alkaline medium. As little as 0·000008 gram of manganese can be detected by this method. No interference with the reaction by iron salts occurs provided a considerable excess of acetic acid is present, and it can therefore be used for the detection of manganese in iron ores and slags. Vogel's thiocyanate reaction for cobalt (*Ber.*, 1879, **12**, 2314) is rendered more sensitive by using acetone instead of either amyl or ethyl alcohols, and quantities of the order of 0·003 mg. of the metal can be detected by this means. G. F. M.

**Separation of Molybdenum and Tungsten by means of Selenium Oxychloride.** HENRY BALDWIN MERRILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2383—2387).—Mixtures of molybdenum trioxide and tungsten trioxide may be quantitatively separated by boiling 1 gram of the mixture with 30 c.c. of a 1 : 1 mixture of selenium oxychloride and concentrated sulphuric acid for sixty minutes. The solution is decanted through a weighed Gooch crucible and the residue washed several times with small quantities of selenium oxychloride and finally brought on to the filter with a hot 10% solution of ammonium nitrate. The crucible is ignited and weighed, and gives the weight of tungsten trioxide, the molybdenum trioxide being obtained by difference. The above method, which is effective for mixtures made by mixing the two oxides by hand, does not work with mixtures of the two oxides precipitated together, if the amount of tungsten trioxide is greater than 10%. In such cases, it is impossible to dissolve all the molybdenum trioxide owing to the formation of solid solutions. This difficulty is overcome by dissolving the oxides in ammonia, adding sufficient nitric acid to precipitate most of the tungsten, evaporating to dryness, and proceeding as described above. The method gives good results. J. F. S.

**Technical Estimation of the Colloidal Part of Tungsten Powder.** A. LOTTERMOSER (*Kolloid Z.*, 1922, **30**, 53—61).—Two methods are described for the estimation of the percentage of colloidal tungsten in commercial tungsten powders. The methods are (1) a sedimentation method, and (2) an optical method, both of which lead to approximately the same results. Sedimentation method: the sample (20 grams) is shaken thoroughly with 100 c.c. of water in a tube and allowed to sediment for two days, 75 c.c. of the supernatant liquid are removed, and 75 c.c. of water added to the sediment. The mixture is shaken and allowed to sediment for a further two days. The process is repeated as long as a measurable quantity of tungsten remains in the supernatant liquid. The sediment is then dried and weighed and gives the non-colloidal portion. The addition of ammonia to the water shows that whilst most specimens of tungsten powder are very finely divided and give suspensions, some only are truly colloidal, inasmuch as they are peptised by ammonia. Optical method: this consists in estimating the quantity of tungsten in the solutions from which the powder has sedimented by means of its absorption of light. The light from a quartz mercury lamp is allowed to pass through the solution on to a potassium photo-electric cell and the absorption determined from the galvanometer deflection. In this connexion, it is shown that the de Beer-Fick law is applicable. Five specimens of tungsten powder have been examined and found to contain respectively 7·5%, 5·5%, 11·25%, 39·75%, and 7·0% of colloidal tungsten. The fourth and fifth samples are peptised by ammonia. J. F. S.

**Separation of Columbium and Tantalum by means of Selenium Oxychloride.** HARRY BALDWIN MERRILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2378—2383).—A method of analysis of mixtures of tantalum and columbium oxides, and for the preparation of the pure oxides is described. The mixed oxides together with titanium oxide if such be present are separated together from the mineral, ignited, and weighed. A sample (0·2—0·3 gram) of the mixed ignited oxides is boiled in an Erlenmeyer flask with 50 c.c. of a 1 : 1 mixture of selenium oxychloride and concentrated sulphuric acid for thirty minutes on a sand-bath, care being taken that clouds of vapour are not evolved. The solution after cooling is decanted on to an asbestos pad in a Gooch crucible and filtered by suction. The filtrate is poured into a large volume of water and boiled, when hydrated columbium pentoxide is precipitated. The residue is boiled with 20 c.c. of the 1 : 1 mixture for fifteen minutes, decanted, and treated as before and the process repeated until the filtrate on hydrolysis gives only a faint cloudiness due to traces of tantalum pentoxide. The residue from the flask is now washed into the Gooch crucible and without much washing the crucible is ignited and weighed; the gain in weight gives the amount of tantalum pentoxide, whilst the loss of weight gives the columbium pentoxide, with titanium if this is present. The method gives results which have a maximum error of 3% and

is therefore better than the Marignac method whilst at the same time being more rapid.

To prepare pure columbium oxide, the mixed oxides are extracted with sufficient solvent to dissolve all the columbium, but it should not be boiled until all the columbium is dissolved, since this would mean the solution of much tantalum oxide. The dissolved oxide is precipitated with water and ammonia, filtered, and ignited. It still contains some tantalum oxide which by repeating the treatment can be removed and very pure columbium oxide obtained. Pure tantalum oxide is prepared by boiling the mixed oxides with the reagent until all the columbium oxide is dissolved; thus whilst sacrificing a little tantalum oxide, a very pure product is obtained. The complete removal of the columbium oxide is hastened by adding a little more sulphuric acid to the 1 : 1 mixture of selenium oxychloride and sulphuric acid. J. F. S.

**The Estimation of Small Quantities of Antimony in Copper and Brass.** B. S. Evans (*Analyst*, 1922, **47**, 1—9).—Five grams of the sample are dissolved in 60 c.c. of nitric acid (*d* 1·2) and 10 c.c. of sulphuric acid and the solution evaporated until it fumes strongly. When cold, the mass is dissolved in 100 c.c. of water, 14 grams of sodium hypophosphite are added, and the solution is heated nearly to boiling whereby the copper is precipitated. The solution is filtered and the precipitate washed with hot water. A further 2 grams of sodium hypophosphite and 100 c.c. of hydrochloric acid are added to the filtrate and the liquid is boiled for fifteen minutes to precipitate any arsenic present. After cooling slightly, 10 c.c. of benzene are added to the filtrate and the liquid is well shaken so that the colloidal arsenic becomes suspended in the benzene layer. The liquid is filtered through a wet filter (to retain the benzene and arsenic) and the latter is washed twice with warm water. The filtrate is heated to boiling and a spiral roll of clean copper foil is dropped in and the boiling continued for one and a half to two hours; the liquid is then poured off, the copper washed rapidly with cold water, covered with water, and treated with 1 gram of sodium peroxide. The liquid is warmed until the deposited antimony has dissolved, then decanted off and the strip washed with cold water. The solution is treated with 0·5 gram of zinc sulphide and, after one and a half to two hours, filtered. The filtrate is acidified with hydrochloric acid, treated with sulphur dioxide, and evaporated to 10 c.c. Five c.c. of standard antimony solution (1 c.c.=0·0001 gram Sb), 80 c.c. of water, and a few drops of hydrochloric acid are treated with sulphur dioxide, and the solution is evaporated to 10 c.c. Both assay and standard solutions are treated with 5 c.c. of 1% gum arabic solution, diluted to 100 c.c., treated with hydrogen sulphide for a few seconds, and transferred to Nessler tubes. The liquid having the greater depth of colour is poured from the glass until the colours match; the depth of the two liquids is measured and the result calculated from these figures. The standard antimony solution is made by dissolving 0·2764 gram

of potassium antimonyl tartrate in 100 c.c. of hydrochloric acid and diluting to 1 litre. A. R. P.

**I. Estimation of Methyl Alcohol in Remains for Forensic Purposes. II. Occurrence of Methyl Alcohol in the Human Body.** H. JANSCH (*Vrtljschr. ger. Med. öffentl. Sanitätsw.*, 1921, **62**, 1—18; from *Chem. Zentr.*, 1921, iv, 983—984).—A weighed portion of the finely divided remains is acidified with tartaric acid and distilled in a current of steam. The distillate (500—1500 c.c.) is repeatedly redistilled, recovering about 60% each time, until a distillate of 5 to 10 c.c. is obtained. Fatty acids are removed by filtration. The later distillations are carried out with alkaline reaction. Acetaldehyde and glycerol which may be present are suitably oxidised. The density and refractive index of the end distillate are determined; from these the amount of methyl alcohol present is calculated, using appropriate tables. For the detection of methyl alcohol, the iodoform, benzoyl chloride, and morphine–sulphuric acid tests are used. Methyl alcohol is a normal constituent of human fæces and urine with mixed diets. It originates probably from pectins in the food. G. W. R.

**Apparatus for the Estimation of Methoxyl Groups.** WILLIAM M. CUMMING (*J. Soc. Chem. Ind.*, 1922, **41**, 20T).—An improved form of apparatus for the estimation of methoxyl groups by Hewitt and Jones's modification of the Zeisel method in which the methyl iodide is absorbed in pyridine, consists of a round-bottomed flask of 250 c.c. capacity with a neck 10 inches long to which a delivery tube is attached by a ground glass joint. A thermometer is provided with its bulb opposite the delivery exit, and a carbon dioxide inlet tube. The delivery tube leads to a narrow bored **U**-tube, one arm of which contains four convolutions, and each convolution a bulb. This absorber holds about 10—15 c.c. of pyridine, and by passing a very slow current of carbon dioxide the whole of the methyl iodide is carried out of the flask and completely absorbed. The thermometer should not register more than 40° (cf. T., 1919, **115**, 1030). G. F. M.

**A Method for the Estimation of Trimethylene Glycol in Crude Glycerol.** L. V. COCKS and A. H. SALWAY (*J. Soc. Chem. Ind.*, 1922, **41**, 17—20T).—The method previously described (*ibid.*, 1918, i, 123, 158T) consisting in the distillation of the crude glycerol and the determination of the specific gravity and acetin value of the distillate, from which figures the trimethylene glycol content was calculated from the known specific gravity and acetin values of the pure substances, gives only approximate results, as no allowance is made for alterations in volume when glycerol, water, and trimethylene glycol are mixed. The specific gravity of a series of mixtures containing known proportions of these three substances has now been systematically determined, and tables and curves have been constructed by means of which the trimethylene glycol content of any glycerol distillate of known gravity and apparent

glycerol content can be deduced. The pure trimethylene glycol prepared for the purpose boiled at 210—211°/760 mm., or 171°/174 mm.; $d_{20}^{20}$=1·0554. The reduction in specific gravity with increasing trimethylene glycol content was fairly regular, and as a simple method for calculating the amount present, apart from reference to the curves, all that is necessary is to divide by the given factor the difference between the observed sp. gr. and the sp. gr. of pure glycerol of the strength indicated by the acetin figure of the mixture. The factor in question increases regularly with the acetin value from 0·00134 per 1% trimethylene glycol for 50% acetin to 0·00179 for 95% acetin value. An accuracy of ±0·2 is claimed. G. F. M.

**Test for Sucrose in the Presence of Dextrose.** LEON A. CONGDON and CHARLES R. STEWART (*J. Ind. Eng. Chem.*, 1921, **13**, 1143—1144).—When a dry mixture of sucrose and dextrose is extracted with hot ethyl acetate, the dextrose dissolves and the sucrose remains insoluble; on cooling the ethyl acetate solution, crystals of dextrose are obtained. W. P. S.

**Clarification of Urines by Zinc Ferrocyanide.** C. CARREZ (*Ann. Chim. Analyt.*, 1922, [vi], **4**, 11—12).—Polemical. The author points out that his method involving the use of potassium ferrocyanide and an excess of zinc acetate (A., 1908, ii, 329) was never intended as a preliminary step for any estimation other than that of glucose in the urine, and Thiéry's criticism (A., 1921, ii, 527) therefore has no point. G. F. M.

**Colour Reaction of Sucrose.** FERDINAND KRYZ (*Öesterr. Chem. Ztg.*, 1921, **24**, 141—142).—When a mixture of 1 c.c. of saturated ammonium nickel sulphate solution, 1 c.c. of sucrose solution, and a few drops of sulphuric acid or hydrochloric acid is boiled, the green colour of the mixture changes to yellow and then to red; this red coloration persists even when the mixture is cooled. The reaction cannot be obtained with less than 0·005 gram of sucrose, but other sugars do not interfere. The coloration is not obtained when nitric acid is used in place of the sulphuric acid or hydrochloric acid. W. P. S.

**Re-testing the 100°-point of the Saccharimeter. II. Preparation of Chemically Pure Sucrose.** ANTON KRAISY (*Z. Ver. deut. Zuckerind.*, 1921, 785—797).—A method of procedure for recrystallising refined sugar from alcohol for the preparation of pure sucrose for purposes of standardisation is described. The product obtained after several successive crystallisations is considered to be free from invert-sugar. Such a product yielded 0·002—0·005% of ash, and reduced 36—38 mg. of copper under the well-known Herzfeld conditions for estimating invert-sugar in sucrose, and 1·5—1·8 mg. under the conditions of the method recently proposed by the author (*ibid.*, 123). [See also *J. Soc. Chem. Ind.*, 1922, 151A.] J. H. L.

**Detection of Formic Acid in Wine.** W. FRESENIUS and L. GRÜNHUT (*Z. anal. Chem.*, 1921, **60**, 457—463).—The wine is acidified with sulphuric acid and extracted with ether; the ethereal extract is then shaken with dilute sodium hydroxide solution, the alkaline aqueous solution is separated, evaporated to dryness, and the residue heated at 130° for one hour to remove any traces of formaldehyde. The residue is dissolved in 10 c.c. of water and the solution treated with 5 c.c. of hydrochloric acid (*d* 1·12) and 0·4 gram of magnesium turnings. After two hours, the mixture is distilled, 5 c.c. of distillate being collected; this distillate is boiled for one minute with the addition of 2 c.c. of milk and 7 c.c. of hydrochloric acid (*d* 1·12) containing a trace of ferric chloride. If the wine contained formic acid or its salts, a violet coloration develops in the mixture. W. P. S.

**Apparatus for Measuring the Hydrogen-ion Concentration of a Solution. Application to the Detection of Mineral Acids in Vinegar.** ANDRÉ KLING, A. LASSIEUR, and (MME) A. LASSIEUR (*Compt. rend.*, 1922, **174**, 165—168).—A compensation electrometric method for measuring hydrogen-ion concentration is described in which a millivoltmeter capable of measuring 1200 millivolts with an accuracy of 1 millivolt is used. The hydrogen-ion concentration of vinegar measured with this apparatus or by the colorimetric method, using thymolsulphonphthalein as indicator, serves as a ready means of detecting the presence of mineral acids. The presence of 0·24% of sulphuric acid in vinegar alters the $p_H$ value at 18° from 2·67 to 1·96. W. G.

**Estimation of β-Hydroxybutyric Acid. Estimation of Acetone Substances in the Urine. Estimation of Acetone Substances in the Blood.** ROGER S. HUBBARD (*J. Biol. Chem.*, 1921, **49**, 351—357, 357—374, 375—384).—A modification of Shaffer's method (A., 1914, ii, 77; 1916, ii, 352) for the estimation of β-hydroxybutyric acid is described, in which the time required for the oxidation is reduced to half an hour. The method is applied to urine after removal of interfering substances by precipitation with basic lead acetate, copper sulphate, and sodium hydroxide. The estimation of acetone plus acetoacetic acid in urine is made more accurate by adding to the technique of Shaffer a distillation from acid potassium permanganate solution. The same method is applied to blood after treatment of the latter with colloidal iron, basic lead acetate, and sodium hydroxide.

It is found that in normal urine the total acetone averages about 2 mg. per 100 c.c., the greater part representing β-hydroxybutyric acid; in blood, the total acetone varies normally between 0·1 and 1·0 mg. per 100 c.c. C. R. H.

**Effect of the Presence of Filter-paper on Permanganate-Oxalate Titrations.** STEPHEN G. SIMPSON (*J. Ind. Eng. Chem.*, 1921, **13**, 1152—1154).—Filter-paper reduces permanganate rapidly, especially when the paper is highly disintegrated. In the titration of calcium oxalate precipitates with permanganate solution, the

precipitate should be washed off the filter-paper with hot water and the paper added only when the titration is nearly complete.
W. P. S.

**The Estimation of *H*-Acid.** HENRY R. LEE (*J. Ind. Eng. Chem.*, 1921, **13**, 1049—1051).—The choice of a diazonium salt for use as a standard solution for the estimation of the hydroxyl group should depend on the stability of the salt in the solution in which it is prepared and in which it is to he used, the completeness of the coupling with the intermediate product in question, and the rate of coupling. Comparative experiments in which *H*-acid was titrated with benzenediazonium chloride and with *p*-toluenediazonium chloride respectively show that the rate of decomposition of diazohenzene is approximately eight times as rapid in acid solution, and one and a half times as rapid in alkaline solution, as that of *p*-diazotoluene. Moreover, the rate of coupling of *p*-diazotoluene is slightly more rapid than that of diazobenzene, whilst the secondary coupling, which is marked in the case of commercial samples of *H*-acid titrated with diazobenzene, is very slight when coupled with diazotoluene, and consequently, in the latter case, the end-point is more definite. The use of *p*-diazotoluene in the estimation of *H*-acid, γ-acid, *J*-acid, *S*-acid, and other naphthol- and aminonaphtholsulphonic acids is recommended. A stock solution of *p*-toluidine hydrochloride is prepared by dissolving 10·7082 grams of pure *p*-toluidine in 40 c.c. of pure concentrated hydrochloric acid, and diluting with water to 1 litre. One hundred c.c. of this solution are placed in a 250 c.c. graduated flask, cooled in ice and salt until frozen, and diazotised with 102 c.c. of *N*/10-sodium nitrite solution. After thirty to forty minutes, this is made up to 250 c.c. with water, and shaken well. This solution should be kept at 0° and protected from light. In carrying out the estimation, 5 grams of dry *H*-acid or 10 grams of press-cake are dissolved in 400 c.c. of water and sufficient sodium hydrogen carbonate to produce a clear solution, and made up to 500 c.c. with water. Twenty-five c.c. of this solution are placed in a 600 c.c. beaker, 200 c.c. of ice-water added, and 2 grams of sodium hydrogen carbonate. This solution is cooled in ice and the diazonium solution is added from a burette, jacketed with ice-water, with good agitation. When the titration is almost finished, about 2 grams of sodium carbonate are added to increase the rate of coupling, and 10—15 grams of salt are added near the end-point. The titration is continued to the point when a spot on filter-paper gives a faint purple ring when spotted with *H*-acid solution. The titration is complete if this purple colour develops again when tested after the solution has been left for five minutes. F. M. R.

**Chlorohydrocarbons and Carbon Chlorides. II. The Knowledge of the Saturation Character of the Di-, Tri-, and Tetra-chloroethylenes.** B. M. MARGOSCHES and RICHARD BARU (*J. pr. Chem.*, 1921, [ii], **103**, 216—226).—The iodine numbers of αα- and αβ-dichloroethylene, trichloroethylene, and tetrachloroethylene are practically zero as determined by the Hübl, Wijs, or other "iodine solution" in which the active agent is iodine

monochloride, and therefore these solvents can be used safely as solvents for fats in the determination of their iodine number. This is in accordance with previous work on the influence of chlorine on the degree of unsaturation of a double bond.

W. O. K.

**Detection of Coconut Oil in Butter.** C. F. MUTTELET (*Compt. rend.*, 1922, **174**, 220—223).—The method is based on the fact that pure butter contains cholesterol but not phytosterol, whilst the vegetable fat contains phytosterol, and the melting points of the acetates of these two sterols differ. The sterols in the butter are precipitated by the addition of 20 c.c. of a 1% alcoholic solution of digitonin to the fatty acids from 50 grams of the butter. The precipitate is collected and washed free from fatty acids by chloroform and ether, and then boiled with 2—4 c.c. of acetic anhydride. The acetate is twice crystallised from alcohol and its melting point determined. The acetate from pure butter has m. p. 113·6—114·2°. With 10% of coconut oil present in the butter the resulting acetate has m. p. 114·5° and the m. p. increases as the percentage of coconut oil in the butter increases. W. G.

**A Simple and Exact Method for the Direct Estimation of Acetaldehyde in the Presence of Acetone.** WILHELM STEPP and ROBERT FRICKE (*Z. physiol. Chem.*, 1921, **116**, 293—301).—To estimate the acetaldehyde, the solution is treated with an excess of alkaline-ammoniacal silver of known strength, the reduced silver is filtered off, and the unreduced silver is titrated in the acidified filtrate with $N$/10-ammonium thiocyanate, using ammonium iron alum as indicator. An accuracy of 0·1 mg. can be obtained. In order to estimate the acetone, the acetaldehyde is removed by boiling with silver oxide or with Fehling's solution, the residual liquid is distilled, and the acetone estimated in the distillate by the Messinger-Huppert method. If acetaldehyde has to be estimated at the same time, a known suspension of silver oxide is used and the residual silver oxide is dissolved in ammonia and estimated volumetrically. S. S. Z.

**Spectrochemical Reaction of Methylfurfuraldehyde and Hydroxymethylfurfuraldehyde Phloroglucides.** TETSUTARO TADOKORO (*J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 52—56; cf. Oshima and Tadokoro, A., 1918, ii, 255).—The difference in the colour reactions of methylfurfuraldehyde and hydroxymethylfurfuraldehyde as phloroglucides was observed by means of the ultra-violet spectroscope. The colour reaction when the two aldehydes are allowed to react with phloroglucin and hydrochloric acid changes with the time and is complete in five minutes. At a half to two minutes after the beginning of the reaction, the two phloroglucides give almost the same absorption band in the visible spectrum (λλ 4200—5000 and λλ 4100—5000), but the methylfurfuraldehyde phloroglucide shows an absorption band in the ultra-violet at λλ 2400—3800. Five minutes after the beginning of the reaction, methylfurfuraldehyde phloroglucide gives an

absorption at λλ 4300—4800, whilst hydroxyfurfuraldehyde phloroglucide shows an absorption band at λλ 5000—5500. G. W. R.

**A Supposed Method for the Quantitative Separation of "Saccharin" from *p*-Sulphaminobenzoic Acid.** WALTHER HERZOG and J. KREIDL (*Oesterr. Chem. Ztg.*, 1921, **24**, 165—166).—A method for the estimation of *p*-sulphaminobenzoic acid in commercial "saccharin" has been described by O. Beyer ("Kontrolle und Herstellung von Saccharin," p. 97), which consists in dissolving the material in a slight excess of ammonia, adding a 50% excess of acetic acid, and keeping for twelve hours. The para-acid is said to be completely precipitated under these conditions, whilst the more strongly acidic "saccharin" remains in solution as undecomposed ammonium salt. Experimental investigation of the method with known mixtures of the two pure substances showed, however, that the results were inaccurate to the extent of 2—3%. For example, in mixtures containing 5 and 25% respectively of para-acid, only 3·33 and 23·11% were found. G. F. M.

**Apparatus for Use in Titrating Intermediates with Unstable Diazo-solutions.** C. P. ATKINSON (*J. Soc. Dyers and Col.*, 1922, **38**, 15—16).—The apparatus is intended for the estimation of intermediates for azo-dyestuff manufacture by titration with standard diazonium solutions.

An iron tripod about thirty inches high supports a circular tin trough containing a supply of ice-water, and inside the trough is a circular glass vessel, with an outlet through the centre of the trough, to contain the supply of diazonium solution. The burette, jacketed with the outer tube of a condenser through which the ice-water flows, is supported by a triangle attached to the three legs of the tripod. In one of the three legs of this support a funnel holder is fitted to receive the waste water as it flows from the jacket and conduct it to the sink. F. M. R.

**Mercury or Water Ureometer for the Estimation of Urea in Urine or in Blood.** RENÉ CLOGNE (*J. Pharm. Chim.*, 1922, vii, **25**, 99—100).—The method of graduation in the usual form of ureometer is modified so that the graduated tube immediately below the inlet tap is very narrow and is marked in twentieths of a c.c. as far as the 2 c.c. graduation, and then in fifths as far as the 25 c.c. graduation. This has the advantage of enabling the same apparatus to be utilised for estimating the small amount of urea usually present in blood, as, if the same quantity is taken as of urine for an estimation, namely, 2 c.c., the reading of the volume of liberated gas will fall within the range of the 0·05 c.c. graduations, and an amount as small as 2·5 grams per litre can be accurately estimated. G. F. M.

**Silicotungstic Acid Applied to the Estimation of Caffeine.** A. AZADIAN (*Bull. Soc. chim. Belg.*, 1922, **31**, 15—18).—Silicotungstic acid gives with caffeine, in the presence of 5% hydrochloric acid, a precipitate having the composition

$$12WO_3,SiO_2,2H_2O,3C_8H_{10}O_2N_4,6H_2O.$$

On ignition, it leaves a residue having the composition $12WO_3,SiO_2$ and the factor for converting the weight of this residue into weight of caffeine is 0·2646. For the estimation, a known volume of an extract containing caffeine is evaporated to a syrup, which is extracted with hot water, the extract being made up to 50 c.c. Sufficient hydrochloric acid is added to bring the acid concentration up to 5% and then a solution of silicotungstic acid is added. The mixture is boiled and then left for twenty-four hours; the precipitate is collected, dried, ignited, and weighed. W. G.

**New Method for the Detection of Thymine.** OSKAR BAUDISCH and TREAT B. JOHNSON (*Ber.*, 1922, **55**, [*B*], 18—21).—The method depends on the conversion of thymine into carbamide, acetylcarbinol, and pyruvic acid, the latter being identified as indigotin. Preliminary experiments show that the action is not influenced by the presence of uracil, cytosine, or sugar.

A solution of sodium hydrogen carbonate in water is treated successively with aqueous solutions of thymine and ferrous sulphate; the mixture is well-shaken with air, which causes the gradual conversion of the white, ferrous hydrogen carbonate into ferric hydroxide. The latter is removed and the filtrate concentrated on the water-bath, when the original odourless solution which does not reduce Fehling's solution acquires a characteristic odour and strong reducing properties, probably owing to a Cannizzarro reaction resulting in the formation of acetylcarbinol and pyruvic acid. The presence of the former is conveniently established by distillation of the liquid and treatment of the distillate with *o*-aminobenzaldehyde; the solution is boiled until the odour of the latter disappears, cooled, acidified with hydrochloric acid, and made alkaline again with sodium hydrogen carbonate. The presence of 3-hydroxy-2-methylquinoline is shown by the blue fluorescence of the solution; the reaction is unusually sensitive. The residue from the distillation contains pyruvic acid, the presence of which is detected by the formation of indigotin after addition of *o*-nitrobenzaldehyde and sodium hydroxide. The dye is extracted with chloroform. The presence of 2—5 mg. of thymine is established readily by the formation of the blue chloroform solution.

H. W.

**Application of Folin and Denis's Phosphotungstic Reaction to the Estimation of Uric Acid in Urine.** THIÉRY (*J. Pharm. Chim.*, 1922, [vii], **25**, 87—92).—All the methods for the estimation of uric acid in urine hitherto proposed have the disadvantage of requiring at least 100 c.c. of urine for each estimation. The author considers that the direct application of Folin's phosphotungstic reagent to urine without any preliminary treatment gives results sufficiently accurate for all ordinary purposes, at least in such cases where the volume of urine at disposal is small. The reagents required are Folin's reagent, a solution containing 120 grams of anhydrous sodium carbonate per litre, and a standard solution of uric acid containing 0·2 part per 1000, prepared by means of mono- and di-sodium phosphate. Into a 100 c.c. graduated tube 1 c.c.

of urine and 2 c.c. of the phosphotungstic reagent are introduced, and into a further series of tubes 1, 2, 3, 4, etc., c.c. of standard uric acid solution are placed, each with 2 c.c. of the reagent. The contents of all the tubes are made up to 40 c.c. with the sodium carbonate solution and, after keeping fifteen minutes, when the blue colour has reached its maximum intensity, the volume is made up to 100 c.c. with distilled water, and the uric acid is estimated colorimetrically by comparison with the standard colours in a Duboscq colorimeter. The results furnished by this method are very close to those given by the present author's volumetric silver method after treatment of the urine with potassium zinc ferrocyanide (A., 1921, ii, 527). G. F. M.

**The Estimation of Purine Bases in Urine.** H. STEUDEL and SUNG-SHENG CHOU (*Z. physiol. Chem.*, 1921, **116**, 223—225).—It is suggested that the filtrate from the second copper sulphate precipitation obtained in Krüger's method for the estimation of the purine bases in urine should after its decomposition with hydrogen sulphide be boiled with magnesium oxide in order to eliminate all traces of ammonia the nitrogen of which might otherwise be ascribed to the purine bases. S. S. Z.

**Electrometric Titration of Azo-dyestuffs.** D. O. JONES and H. R. LEE (*J. Ind. Eng. Chem.*, 1922, **14**, 46—48).—The difficulties encountered in the analysis of azo-dyestuffs with titanous chloride by previous methods are enumerated, and an analytical procedure is described whereby the electrometric method of following oxidimetric reactions (cf. A., 1919, ii, 471, 480) is used in conjunction with titanous chloride for the analysis of azo-dyestuffs and nitro-compounds.

A sample of the finely powdered dye (0·5—1·0 gram), sufficient to require 30—45 c.c. of *N*/4-titanous chloride for reduction, is placed in a reaction flask with 25 c.c. of distilled water, and heated on a steam-bath for ten minutes to dissolve or soften the particles. Twenty-five c.c. of 40% sulphuric acid are added, the flask is stoppered, and a current of carbon dioxide is passed through for five minutes; 35—50 c.c. of titanous chloride, being at least 5 c.c. of *N*/4-titanous chloride in excess of that required for reduction, are added, the mixture is boiled for five minutes, and cooled to 30°. In the back titration, the potentiometer is adjusted, and the voltages read for each addition of *N*/20-ferric alum solution. The latter is added in 5 c.c. portions at first, gradually decreasing to 0·1 c.c. or less. When passing over the end-point, the poles are reversed in the usual manner, and the voltages read as the additions of ferric alum become larger. Volts are plotted as ordinates and c.c. of ferric alum solution as abscissæ, and the end-point is determined from the curve. For routine analysis, almost all azo-dyestuffs can be analysed with sufficient accuracy without reading the voltmeter or plotting a curve. The potentiometer is adjusted at the beginning of the back titration, until, on closing the circuit, the galvanometer shows no deflection. A permanent large swing of the galvanometer is obtained at the end-point. F. M. R.

**Estimation of the Percentage of Fibrin in Blood and Plasma.** H. C. GRAM (*J. Biol. Chem.*, 1921, **49**, 279—295).—Citrated plasma is recalcified and heated at 35° for one and a half hours; the clot is then washed and dried, treated with alcohol and ether to remove lipoids, and weighed. The whole estimation, including the platelet count and the cell volume, is performed on 4·5 c.c. of blood.

E. S.

**Chemical Blood Analysis. III. The Importance of the Ultra-filtration Method for the Analysis of Blood.** M. RICHTER-QUITTNER (*Biochem. Z.*, 1921, **124**, 106—113).—Examples are given of the use of the Zsigmondy-Haen ultra-filtration apparatus for the estimation in blood of residual nitrogen, uric acid, chloride, sodium, free potassium, and calcium. The residual nitrogen, the uric acid, the chloride, and sodium are completely dialysable, but only a portion of the potassium, calcium, or dextrose is free and dialysable. H. K.

**Colorimetric Estimation of the Concentration of Hydrogen Ions in Very Small Quantities of Blood by Dialysis.** J. LINDHARD (*Compt. rend. Trav. Lab. Carlsberg*, 1921, **14**, No. 13, pp. 13).—A modification of the method of Dale and Evans (A., 1921, i, 142), in which the required quantity of blood is reduced to three drops, so that the process can be applied repeatedly by finger pricks. Hirudin is used, and phenolsulphonephthalein as indicator. The dialysate is not titrated but compared with a colour scale of phosphate-indicator mixtures. The error for the dialysis of phosphate mixtures compared with a separate scale is about $P_H$ 0·02, but compared with the original mixture the $P_H$ agrees in the second place of decimals. Bicarbonate solutions gave by the electrometric method a $P_H$ 0·2 to 0·3 higher than by the colorimetric, but this discrepancy the author attributes to loss of carbon dioxide in dialysis and inapplicability of the electrometric control (cf., however, Evans, A., 1921, i, 904). G. B.

**Preparation of Colloidal Gold Solution for Testing Spinal Fluid.** A. O. GETTLER and J. W. JACKSON (*Arch. Neurol. Psychiatry*, 1921, **6**, 70—71).—To one litre of water (distilled in copper vessels from potassium permanganate) are added in turn 10 c.c. of 1% auric chloride solution, 7 c.c. of 2% potassium carbonate solution, and 0·5 c.c. of 1% oxalic acid solution. The liquid is heated until it boils, then removed from the flame and vigorously shaken, 0·2 to 0·3 c.c. of concentrated formaldehyde solution being simultaneously added, and the shaking continued for one minute; after three or four minutes, the colour usually commences to develop. If it does not do so, an additional 0·1 to 0·2 c.c. of formaldehyde solution is added, with agitation during and after the addition. A deep red colour should rapidly develop. CHEMICAL ABSTRACTS.

## General and Physical Chemistry.

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**Relation between Atomic Volumes [of Elements in Combination] and Optical Refractivities.** GERVAISE LE BAS (*Nature*, 1921, **108**, 272—274).—A periodic relationship is known to exist between the atomic volumes of elements in combination, the differences between the atomic volumes of successive members of the same series being of the order of that of hydrogen. Similar serial and group relations are observed with the atomic refractivities, the serial differences again being of the order of the atomic refractivity of hydrogen. When the atomic volumes of carbon, nitrogen, oxygen, fluorine, silicon, phosphorus, sulphur, chlorine, arsenic, selenium, bromine, and iodine are plotted against their atomic refractivities, the points obtained lie approximately on a straight line. A. A. E.

**Molecular Refraction of some Molten Salts and their Degree of Dissociation.** G. MEYER and HECK (*Z. Elektrochem.*, 1922, **28**, 21—23).—The molecular refraction of molten sodium hydroxide and nitrate and potassium hydroxide and nitrate has been measured at a series of temperatures between 320° and 440°. The method adopted was to allow a ray of light (sodium) to fall into a prism of the molten substance and be reflected from a metallic mirror inside the prism. The densities of the molten salts were determined for all the temperatures used. The mean molecular refraction over the whole temperature range is found to be : sodium nitrate 11·54, potassium nitrate 14·09, sodium hydroxide 5·37, and potassium hydroxide 7·71. These values, which are accurate to one unit in the second decimal place, the refractive index being accurate to one unit in the third decimal place, are in good agreement with the values calculated from the atomic refractions. Using the values 2·80 and 2·59, respectively, for the atomic refractions of the sodium atom and the sodium ion, it is calculated that molten sodium nitrate is dissociated to 61·7%. The influence of temperature on the molecular refraction of all the substances examined is very small. J. F. S.

**Some Problems of the Mass Spectrograph.** F. W. ASTON and R. H. FOWLER (*Phil. Mag.*, 1922, [vi], **43**, 514—528).—A mathematical discussion of some points raised by the performance and further design of the mass spectrograph. J. R. P.

**The Broadening of Spectral Lines.** J. FRANCK (*Festschrift Kaiser Wilh. Ges. Ford. Wiss. Zehnjährigen Jubiläum*, 1921, 77—81).—A summary of the manner in which the broadening of spectral lines has been explained, or is capable of explanation, both by classical methods and in terms of the quantum theory. Radiation damping has been fairly adequately explained on the quantum

theory by Stern and Volmer; the Döppler effect may be explained by the influence of radiation pressure, whilst collision damping is considered to be due to the electron transitions produced by a collision, together with a sudden warping of the electron orbits.
CHEMICAL ABSTRACTS.

**Intensity and Broadening of Spectrum Lines.** CHR. FÜCHTBAUER and G. JOOS (*Physikal. Z.*, 1922, **23**, 73—80).—The form of a spectrum line broadened by another gas depends on the latter, not on the absorbing gas. The constant representing the broadening is, with hydrogen and nitrogen, proportional to the density. In the first pair of the principal series of cæsium, the number representing the dispersing electrons on the classical theory is equal to the number of cæsium atoms. For the mercury line 2537, the number of resonators is one forty-fifth of the number of atoms. The maximum of 2537 is less displaced towards the red by hydrogen than by carbon dioxide and nitrogen. J. R. P.

**Excitation Stages in Open Arc-light Spectra. I. Sodium, Potassium, Calcium, Strontium, Barium, and Magnesium. II. Silver, Bismuth, Cadmium, Zinc, Air, and Copper.** B. E. MOORE (*Astrophys. J.*, 1921, **54**, 191—216, 246—272).—An investigation of the variation of the spectrum with current, using a potential of 2000 volts and currents of 0·02 to 1 ampere, distinguishes between five stages of excitation; the features of each are described, and a number of intensity–current curves are given. The relation of the results to previous work, including the Bohr theory, is briefly discussed. A. A. E.

**Influence of the Pressure of Foreign Gases on the *D*-Lines in Saturated Sodium Vapour.** R. MINKOWSKI (*Physikal. Z.*, 1922, **23**, 69—73).—Measurements of the magnetic rotation of the *D*-lines of sodium vapour in presence of nitrogen under various pressures showed that the constant representing, on the classical theory, the number of dispersion electrons in unit volume is affected by pressure. The difference in the values of this constant determined by absorption measurements and extrapolated from the magnetic rotations is largely, perhaps entirely, to be ascribed to the influence of pressure. The broadening of the lines under the influence of pressure is largely confined to the side near the red. The method may be used in the determination of small partial pressures of monatomic vapours in mixtures. J. R. P.

**The Production of Enhanced Line Spectra.** R. A. SAWYER and A. L. BECKER (*Science*, 1921, **54**, 305—306).—When calcium wires are exploded by the Anderson method (*Astrophys. J.*, 1920, **51**, 37), it is found that, as the size of the wires employed is decreased, the energy of the stimulus remaining the same, the intensity of the enhanced lines is increased, indicating a more complete ionisation of the calcium atoms. A fine asbestos fibre about 3 cm. in length was therefore saturated with an aqueous

olution of a calcium salt, and the charge of the high-tension con- lensers thrown across it. The fibre remained uninjured, and the alcium spectrum thus produced showed a striking enhancement ıf the spark lines of calcium over the arc lines, indicating that a arge proportion of the emitting atoms were ionised. A table ;iving the relative intensities, under various conditions, of prominent park- and arc-lines of calcium shows that the new source of light, ›rovisionally called the "super-spark," yields a degree of ionisation 'omparable with, or perhaps in excess of, that existing in the high ·hromosphere of the sun and in the early (or hot) type *B* stars. ⁄ery minute amounts of material suffice for the production of ntense spectra by this method, and practically only metallic lines ıre produced; the spectra of hydrogen, oxygen, or of the acid 'adicle of the salt used do not appear, and only the strongest air ines could be observed. A. A. E.

**The Evolution of the Spectrum of Magnesium under the** **nfluence of Increasing Electric Fields. Applications to** **Astrophysics.** A. DE GRAMONT and G. A. HEMSALECH (*Compt. ·end.*, 1922, **174**, 356—361).—In a discussion of previous work A., 1921, ii, 611), it is shown that the spectral effects of intense ·lectric fields are particularly marked in the initial stage of a uminous phenomenon (arc or spark) when the temperature and he electrical conductivity of the vapours are not very high. As ·he temperature increases, the emission, which depends on rapid 'alls in potential, diminishes or disappears. In consequence, the ıuthors consider it dangerous to conclude that a star has a high emperature because the spark rays predominate in its spectrum.
W. G.

**The Lines $K_a$ of the Light Elements.** V. DOLEJSEK (*Compt. end.*, 1922, **174**, 441—443).—The author has again measured the $K_a$ lines of the elements from zinc to chlorine. He has found for hese elements the lines $\alpha_3$ and $\alpha_4$ which Hjalmar had measured or the elements sulphur to sodium. They are inseparahle above candium. The line $\alpha_7$, according to Siegbahn's notation, was ılso found for the elements calcium to chlorine. In addition, a ıew satellite of $\alpha_1$ of shorter wave-length has been found. It ıppears to be an emission band, and is denoted by $\alpha_1'$. The line $\alpha_3$ ound by Duane and Stenström for tungsten could not be observed.
W. G.

**The Complexity of the *K* Series of the Light Elements** **ınd its Theoretical Interpretation.** A. DAUVILLIER (*Compt. end.*, 1922, **174**, 443—445).—Ten components of the *K* series or copper have previously been reported. Their wave-lengths ıre now recorded. Working under the same conditions (cf. A., 921, ii, 669), the *K* series of molybdenum has been studied without ›bserving any rays other than those found by Duane. The line $\alpha_3$ ound by Duane for tungsten does not exist either for copper or nolybdenum. An attempt is made to show the relationship

between the author's measurements of the rays $\alpha_7$, $\alpha_3$, and $\alpha_4$ copper and those of Hjalmar for the elements calcium to sodium.
W. G.

**Wave-lengths Longer than 5500 Å. in the Arc Spectra Yttrium, Lanthanum, and Cerium, and the Preparation Pure Rare Earth Elements.** C. C. Kiess, B. S. Hopkins, a H. C. Kremers (*U.S. Bureau of Standards, Sci. Papers*, 19 No. 421, 318—351).—Photographic determinations were made the yellow, red, and infra-red regions of the arc spectra, as follow yttrium, 170 lines to 7881·868 Å., lanthanum, 410 lines to 9078· Å., cerium, 1700 lines to 9024·68 Å. A description is given of t methods used in the purification of the substances employed, co pounds of cerium, samarium, lanthanum, neodymium, and ga linium being obtained from a sample of "Welsbach" sodium ra earth sulphate, and those of yttrium, dysprosium, and erbium fr gadolinite and xenotime. The cerium was removed from t "Welsbach" residues by precipitation with potassium bromate basic ceric bromate; the other elements were then separated way of the fractional crystallisation of the double magnesiu nitrate. The yttrium-group material was freed from the eleme of the cerium group, and then fractionally crystallised as broma
Chemical Abstracts.

**The *L* Series of the *X*-Ray Spectrum.** D. Coster (*Com rend.*, 1922, **174**, 378—379).—The author has again measured t spectra of a large number of elements (tantalum to rubidiu and in general the new results confirm the conclusions of previo work and in addition lend support to Bohr's theory of the structu of the atom (cf. this vol., ii, 277). Certain of the author's results a more or less opposed to the results and conclusions of Dauvilli (cf. A., 1921, ii, 421, 475, 699) and these divergences are summarise
W. G.

**The Infra-red Absorption Spectra of Alkali Hydroxide** G. E. Grantham (*Physical Rev.*, 1921, **18**, 340; cf. Howe a Gibson, *ibid.*, 1917, **10**, 767).—When the absorption of solutio of sodium, potassium, and lithium hydroxides (of various conce trations) and of ammonium and cæsium hydroxides (one soluti each) was determined with reference to that of water, all the curv showed a broad, intense absorption band with a maximum about 2·29$\mu$, except in the case of the ammonium hydroxi solution, for which the maximum was found to be at 2·20$\mu$. T absorption was found to be proportional to the concentration, b not to vary systematically with the atomic weight of the met used. It is suggested that the band is due to dissociated hydroxi ions, although in the case of other hydroxide solutions such a ba has not previously been observed. Maximum absorption of wat was observed at 1·48 and 1·98$\mu$. The effect of dissolving an alk hydroxide is to decrease the absorption of the water in the band 1·48$\mu$ by an amount proportional to the concentration of the soluti and to the atomic weight of the metal of the base. A. A. E.

**The Ultra-violet Absorption Spectra and the Optical Rotation of the Proteins of Blood Sera.** S. JUDD LEWIS (*Proc. Roy. Soc.*, 1922, [*B*], **93**, 178—194; cf. A., 1917, ii, 62).—Eleven sera, six from the horse and five from man, were used for the separation and purification by modifications of well-known methods of the albumin, euglobulin, and ψ-globulin. The optical rotation and the ultra-violet absorption spectra of the individual proteins were examined in detail. ψ-Globulin, euglobulin, and albumin from horse sera had specific rotations of −52°, −43°, and −57·4°, respectively, the corresponding values for human being −46° and −48° for the globulins and varying values for the albumin. The absorption curves are similar in form and character to that of serum, well-developed bands being best found at concentrations of 0·08% for alhumin and 0·04% for the globulins. The absorption curve of ψ-globulin is the same for the horse and man and differs from euglobulin in the extinction coefficients but not in general form. For horse and human albumin, the curves are the same except for a constant ratio in their magnitudes, due possibly to physical or chemical association of an aggregate of little or no absorptive power. H. K.

**The Fluorescence of Mercury Vapour.** J. S. VAN DER LINGEN and R. W. WOOD (*Astrophys. J.*, 1921, **54**, 149—160).—Since the fluorescent spectrum of mercury vapour cannot be excited in quiescent vapour, but only in vapour which is being distilled from the metal at a temperature not less than 150°, the active molecules are presumably not neutral monatomic molecules, but others, possibly diatomic, present only during distillation. The spectrum consists of lines at 2536, 2539, and 2346 Å., and four structureless bands with maxima at 2346, 2540, 3300, and 4850 Å. The complete spectrum is excited by light from a zinc spark, but single lines excite only a part. The relation of the spectrum to the exciting light is examined in some detail. A. A. E.

**Hydrates of Boron Trioxide as a Constituent of Systems Capable of Strong Phosphorescence and containing Organic Compounds.** ERICH TIEDE and PETER WULFF (*Ber.*, 1922, **55**, [*B*], 588—597).—The phosphorescence of partly dehydrated boric acid (A., 1921, ii, 75) originates from traces of organic compounds, is removable, not by recrystallisation, ignition in a stream of oxygen, boiling with nitric acid, or fusion with potassium nitrate, but by boiling with fuming nitric acid for twenty-four hours, subsequently recrystallising three times from water specially purified, and finally igniting the upper portion of the filtered mass (which had not been in contact with filter-paper) in a platinum crucible. Phosphorescence could not be induced in such a product by any means other than by introduction of organic impurities. For this purpose, even those present in ordinary distilled water suffice. A number of fluorescent boric acid compounds were prepared by the respective additions to purified boric acid of fluorescein, its sodium salt (uranin), phenolphthalein, benzoic acid, quinone,

aniline, dimethylaniline, diphenylamine, phenol, quinol, naphthol, terephthalic acid, pyridine, and quinoline—in short, aromatic or heterocyclic compounds, but not aliphatic compounds, unless these (for example, ethylene glycol or sugar) undergo some decomposition—followed by fusion of the mixtures to transparent glasses, or by heating for two hours in the vacuum of a water-pump until a partly sintered mass is produced. Inorganic compounds, even those of uranium or the platinocyanides, with the exception of boron nitride (Tiede and Büscher, A., 1921, ii, 74) do not produce phosphorescent materials, nor can the boric acid be replaced by silicic or phosphoric acids. Hydration to orthoboric acid consequent on exposure of the products to air largely destroys the phosphorescence, as does also too intense dehydration. Phosphorescence is excited by daylight, but usually best by the ultra-violet light of the quartz lamp, and does not usually persist for more than two minutes. The intensity, however, is frequently much greater than that from the phosphorescent alkaline earths and sufficient momentarily to illuminate comparatively large spaces. Blue tones predominate, but reddish-yellow and green effects have been observed. Röntgen, cathode, and radium rays have no effect. The new products show only slight tendency towards thermoluminescence, down to the temperature of liquid air. In common with analogous cases, they are produced when the medium (boric acid) suffers contraction. They offer no support for the view that luminescence of organic compounds is dependent on their slow decomposition (Perrin, A., 1918, ii, 418; 1919, ii, 177). Pure anthracene, in spite of its fluorescence, causes no fluorescence in boric acid, but compounds like ethyl dihydrocollidinedicarboxylate, which are excited by radium rays, give a product in which fluorescence is produced by ultra-violet illumination, but is indifferent to radium. It is presumed that the phosphorescence emanates from definite organic derivatives of boric acid (cf. Dimroth and Faust, A., 1922, i, 155; Pictet, A., 1903, i, 601). Thus orange crystals result from evaporation of a solution of boric acid containing uranin (1 : 3000), but these, on fusion, become light green and simultaneously acquire capacity for phosphorescence.

J. K.

**Action of Red and Infra-red Rays on the Phosphorescent Sulphides.** MAURICE CURIE (*Compt. rend.*, 1922, **174**, 550—553).—As an explanation of the extinguishing action of the less refrangible part of the spectrum on certain phosphorescent substances, it is suggested that the action of the extinguishing rays will consist in rendering the medium a conductor by the detachment of electrons from the atoms of sulphur, in the case of the sulphides. In support of this theory, experiments are described in which an increase of conductivity was found for finely-powdered sulphur and certain sulphides when they were exposed to the action of red rays. This hypothesis also gives an explanation of the fact that the extinguishing action is not limited to the red and infra-red portions of the spectrum.

W. G.

**Preparation of Phosphorescent Magnesium Sulphide.** ERICH TIEDE and FRIEDRICH RICHTER (*Z. Elektrochem.*, 1922, 28, 20—21).—Strongly phosphorescent preparations of magnesium sulphide containing small quantities of bismuth, antimony, or manganese may be prepared. These substances exhibit a violet, golden-yellow, or dark red phosphorescence and an afterglow which in every way corresponds with that of the well-known preparations of the alkaline earth sulphide. Details of the method of preparation of phosphorescent magnesium sulphide are not given in the paper.

J. F. S.

**Experimental Proof of some Theories of Natural Rotatory Power of Optically Active Solutions.** PAUL WETTERFORS (*Z. Physik*, 1922, 8, 229—242).—With the object of testing the hypotheses of optical rotation put forward by Lorentz and Livens ("Theorie elektr. opt. Erscheinungen," 1906; A., 1913, ii, 543; 1914, i, 830), the author has measured the specific rotation, $[\alpha]$, the refractive index, $n$, and the rotatory dispersion of solutions of camphor in ethyl alcohol, propyl alcohol, acetone, benzene, and toluene, and of $\alpha$-bromocamphor in the three last-named solvents. The measurements were made with solutions of various concentrations from 10·02 to 49·98 grams per 100 c.c. of solution at temperatures from 11·1° to 18·0°. Four series of measurements were made in each case with light of wave-lengths $589\mu\mu$, $546\mu\mu$, $436\mu\mu$, and $710\mu\mu$, the first being obtained from a sodium lamp and the three latter from a quartz mercury lamp by the use of suitable light filters. The specific rotation of $\alpha$-bromocamphor in acetone solution in various concentrations, $c$, is given by the equations $[\alpha]_{\lambda=710}=86{\cdot}87+0{\cdot}0625c$; $[\alpha]_{\lambda=589}=140{\cdot}08+0{\cdot}1043c$; $[\alpha]_{\lambda=546}=172{\cdot}01+0{\cdot}1389c$; $[\alpha]_{\lambda=436}=350{\cdot}25+0{\cdot}3561$. It is shown in general the rotation increases with increase of temperature, since the concentration of a solution decreases with increasing temperature the specific rotation is also greater. An exception is found in the case of acetone solutions of $\alpha$-bromocamphor; here the rotation decreases with increasing temperature, but the specific rotation is independent of temperature. The rotatory dispersion, defined as the ratio $[\alpha]_\lambda : [\alpha]_{589}$ where $[\alpha]_\lambda$ is the specific rotation for the wave-length $\lambda$ and $[\alpha]_{589}$ the same quantity for $\lambda=589$, changes in general with the concentration. Bromocamphor shows an increase, camphor a decrease for the wave-lengths $\lambda=546\mu\mu$ and $436\mu\mu$ ($\lambda>589\mu\mu$), but for $\lambda=710\mu\mu$ ($\lambda<589$) an increase when the concentrations are greater. Solutions of camphor in acetone are exceptional, for here the rotatory dispersion is constant. According to Livens's theory, the expression $[\alpha]=r\nu^2/2\,.\,(n^2-1)[a(n^2-1)+1]$ must hold; this has been rewritten in the form $[\alpha]=ay_0(n^2-1)^2+y_0(n^2-1)$, where $y_0=r\nu^2/2$. On plotting the values of $[\alpha]/(n^2-1)$ against $(n^2-1)$, a straight line should be obtained. Treating the present experimental values in this way actually leads to straight lines for solutions of camphor in benzene and toluene, and for bromocamphor in benzene; in all other cases a straight line passes only approximately through the points. The values of $a$ and $y_0$

have been evaluated by the method of least squares, and it is show that the value of $a$ is always negative as shown by Peacock (T 1914, **105**, 2782; 1915, **107**, 1547). The numerical values of are largest for bromocamphor in toluene and benzene and smalle for camphor in ethyl alcohol. The $a$ value for camphor in toluen is the same for $\lambda=546\mu\mu$ and $\lambda=436\mu\mu$. It is shown, therefor that the Lorentz-Livens hypothesis can only claim to give qualitativ representation of the present material. According to Oseen hypothesis, the expression $k=[\alpha]:(n^2+2)^2$ must be constant. Th experimental data show that this is not the case, for in the cas of solutions of camphor in benzene, toluene, and the alcohol the $k$ value increases with increasing concentration, but decrease with acetone solutions. Further, except in the case of solution of camphor in propyl alcohol, the value of $k$ is a linear functio of the concentration. J. F. S.

**Photochemical Studies. XIV. Fundamental Photochem cal Laws.** J. Plotnikow (*Z. wiss. Photochem.*, 1922, **21**, 134-140).—A theoretical paper in which Einstein's photochemic equivalent law and the Grotthus–van't Hoff photochemical absorp tion law are critically examined. It is shown that Einstein law leads to the following improbabilities. On calculating th energy absorbed, by one gram molecule, from light of vario wave-lengths, it is found that the extreme ultra-violet, $100\mu$, gives up 300,000 cal. and Röntgen rays $3\times10^9$ cal., which indicat that with decreasing wave-length light becomes much more activ until, with Röntgen rays, all molecules will be simply destroye Further, all atoms in all reactions in all solvents must react wit the same velocity at all temperatures and must take up the sam quantity of energy. It is shown that the Grotthus–van't Ho law is diametrically opposed to the Einstein law. Nine class of photolytic reactions are quoted in which the Einstein law no way represents the facts, and two further classes are noted which deviations from the law of $-8\%$ to $22\%$ are observe The photolysis of hydrogen iodide and hydrogen bromide alo give an approximate agreement, but here there is a divergen varying between $-3{\cdot}3\%$ and $+4\%$. Weigert's recent pap (*Z. Physik*, 1921, **5**, 421), which shows the applicability of th Einstein law and characterises the Grotthus–van't Hoff law a untenable, is criticised. It is shown that the reactions studie and the method of operation is much too complicated to mak it possible to draw conclusions of the type drawn by Weigert fro the results. In the present author's opinion, the Einstein law i its present form cannot be maintained. J. F. S.

**Photosynthesis and the Electronic Theory. II.** Henr H. Dixon and Nigel G. Ball (*Sci. Proc. Roy. Dubl. Soc.*, 192 **16**, 435—441; cf. Dixon and Poole, A., 1920, ii, 343).—In con tinuation of previous work, the photo-electric properties of chloro phyll were investigated. The electronic theory of sensitisatio is supported by experiments in which sensitised photographi plates were affected by light at a temperature of $-185°$, chemic

ction being thereby precluded. Using collodion films, it was hown that sensitisation by chlorophyll is also effective even at he temperature of liquid air. Since only light of visible wave-engths is absorbed by chlorophyll, and since earlier experiments ave shown that electrons are not expelled from chlorophyll, it ollows that the light absorbed is wholly used in the displacement f electrons within the molecule, thereby making some atomic roup or groups reactive. In photosynthesis, these groups may eact with carbon dioxide and water, according to the scheme hlorophyll-$a+CO_2$=chlorophyll-$b+CH_2O$ and chlorophyll-$b+H_2O$=chlorophyll-$a+O_2$. It is assumed that these reactions nly take place during illumination and depend on its intensity. The velocity of the first reaction would only increase with intensity f illumination so long as carbon dioxide is in excess, whilst the elocity of the second reaction would only be indirectly influenced y this factor. G. W. R.

**Absorption of Röntgen Rays.** K. A. WINGÅRDH (*Z. Physik*, 1922, **8**, 363—376).—A method for the determination of the absorption coefficients of substances in solution for the homogeneous Röntgen rays of the $K_\alpha$ line of molybdenum is described. The atomic absorption coefficients are calculated, and it is shown that the logarithms of these when plotted against the logarithms of the ordinal numbers of the elements give two straight lines. Oxygen showed a marked deviation. J. R. P.

**Spark Lines in the Röntgen Spectrum.** GREGOR WENTZEL (*Ann. Physik*, 1921, [iv], **66**, 437—461).—It is assumed that the inner shells of the atom may under certain conditions undergo repeated ionisation. By the spontaneous transition of an atom from such a state to a state of equal level, Röntgen lines will be emitted which correspond with spark lines in the optical spectrum. It is shown that the emission can have only one fine-structure of known Röntgen lines, which is extended usually towards the region of short wave-lengths. All the lines which previously caused difficulty in the systematic arrangement of Röntgen spectra can be regarded as spark lines; in particular the hard $K\alpha$ satellites, from $K\alpha_3$ to $\alpha_6$ can be derived from two combination relations, and the complex structure of the $K$-absorption edges observed by Fricke is also elucidated. The magnitudes of the frequency differences and their linear change with ordinal number are satisfactorily explained. J. R. P.

**X-Rays and Thermodynamic Equilibrium.** L. DE BROGLIE (*J. Phys. Radium*, 1922, [vi], **3**, 33—45).—The conditions of thermodynamic equilibrium between atoms, electrons, and radiation in an enclosure maintained at a temperature $T$ are considered. The statistical equilibrium between the atoms is described by the law of Maxwell and Boltzmann, which may be applied to systems in which the total energy may assume only a certain number of discontinuous values. The equilibrium density of

radiation in the region of frequencies considered may be represented by Wien's law. The free electrons are considered as forming an ideal gas, with density proportional to $T^{\frac{3}{2}}$. The atomic coefficient of absorption of a substance is then shown to be given by $\mu = C\lambda^3\Sigma_p n_p E^2{}_p$, where $C$ is a constant, $\lambda$ the wave-length, $n_p$ the number of electrons in the level $p$ (in the sense of Bohr's theory), and $E_p = h\nu_p$ the energy emitted when the atom passes from the ionised to the normal state. This result is compared with experiment. J. R. P.

**Stopping Power and Atomic Number.** J. L. GLASSON (*Phil. Mag.*, 1922, [vi], **43**, 477—481).—By a discussion of known results it is shown that the stopping power of an atom is proportional to $N^{\frac{2}{3}}$, where $N$ is the atomic number, rather than to $A^{\frac{1}{2}}$, where $A$ is the atomic weight, as previously supposed. This agrees with the higher stopping power of hydrogen as compared with helium. J. R. P.

**Isotopy of the Radio-elements.** M. L. NEUBURGER (*Nature*, 1921, **108**, 180).—Meitner's (this vol., ii, 15) nucleus model of the radio-elements permits of the division of the radioactive isotopes into four classes: (1) those which possess only the same nuclear charge and the same arrangement of their outer electrons, for example, radium and mesothorium-I, (2) those which have in addition the same atomic weight and the same total number of nuclear "building stones," for example, ionium and uranium-*Y*, (3) those having the same number of each nuclear building stone, but a different arrangement of these in the atomic nucleus, for example, radium-*D* and actinium-*B*, (4) those possessing the same arrangement of building stones, and thus the same probability of disintegration, for example, radium-*G* and actinium-*D*. Such elements cannot at present be designated isotopes since there is no available means of distinguishing between them. A. A. E.

**The Ionium Content of Radium Residues.** ELIZABETH RONA (*Ber.*, 1922, **55**, [*B*], 294—301).—Ionium has been estimated in various radium residues according to the "indicator" method with the aid of uranium-*X* and the content has been compared with that of pitchblende. The final residues obtained during the extraction of radium in Austria still contain approximately 16% of the ionium present originally in the pitchblende. Thorough extraction of the latter with nitric acid on a laboratory scale gives insoluble residues which are almost completely free from ionium.

The importance of the estimation of ionium for that of protoactinium in uranium minerals and for the inter-relationships of the actinium series is discussed. H. W.

**Artificial Disintegration of the Elements.** A Lecture delivered before the Chemical Society on February 9th, 1922. SIR ERNEST RUTHERFORD (T., 1922, **121**, 400—415).

**Luminescence of Flame Ions in the Air Spark.** H. GREINACHER (*Physikal. Z.*, 1922, **23**, 65—69).—When a flame coloured

with a salt vapour is brought into a strong electric field, the ions may be caught on two platinum wires, outside the flame, on which they may afterwards be detected spectroscopically by heating. When a spark is passed between a wire in the flame and a brass sphere a few centimetres from the flame, or two wires similarly placed, the spectrum of the spark shows the lines of hydrogen and the metal ions. Lithium, sodium, potassium, rubidium, cæsium, thallium, and strontium were examined. The metals move principally to the negative electrode, but partly to the positive. In the case of strontium, all the lines leave the flame, but in the other cases only a limited number. In spite of the strong field in the spark, only the lines with a small exciting potential (small $h\nu$) appear. The ions are partly produced in the flame and partly in the spark. An apparent change in wave-length occurs.

J. R. P.

**Ionic Equilibria on Metallic Surfaces.** H. VON EULER [with ARVID HEDELIUS and ZIMMERLUND] (*Z. Electrochem.*, 1922, **28**, 2—6).—An account is given of the sorption of gold, silver, and mercury ions on the surfaces of the metals. The method consisted in determining analytically the change in the concentration of solutions of silver nitrate and silver sulphate after they had been in contact with metallic silver and gold respectively. Similar experiments are described for solutions of mercuric chloride in contact with mercury. It is shown that 1 sq. metre of silver surface absorbs 0·35 mg. ion from silver nitrate and 0·5 mg. ion from potassium chloride solution, whilst the same area of gold absorbs 0·063 mg. ion from silver nitrate. A sq. metre of mercury surface absorbs 0·004 mg. ion from mercuric chloride solution. The results are discussed in connexion with the charge of an electric double layer. J. F. S.

**Evidence for the Existence of Homogeneous Groups of Large Ions.** P. J. NOLAN (*Physical Rev.*, 1921, **18**, 185—198).—Using, as did Blackwood (*ibid.*, 1920, **16**, 85), the Zeleny method for the measurement of the mobilities of ions, instead of that previously employed by McClelland and Nolan (*Proc. Roy. Irish Acad.*, 1919, **35**, [*A*], 1, and previous papers), evidence has been adduced to confirm the author's original statement that when large ions are produced in air in various ways, the ions can be divided into a number of groups, each group having a definite mobility. It is considered that Blackwood's negative results were due to ions changing from group to group when the time spent in the measuring chamber is relatively long. A. A. E.

**The Scattering of Electrons by Nickel.** C. DAVISSON and C. H. KUNSMAN (*Science*, 1921, **54**, 522—524).—When a nickel target is bombarded by a stream of electrons, there is observed, besides the emission of slowly moving secondary electrons characteristic of all metals, an appreciable emission of electrons of higher speed. After experimental and mathematical examination of

the phenomenon, it is suggested that the sharp deflexions experienced by these scattered electrons must result from their penetration into the atomic structure and their deflexion by the strong field which they encounter. A. A. E.

**Dielectric Constants of some Esters at Low Temperatures.** L. C. JACKSON (*Phil. Mag.*, 1922, [vi], **43**, 481—489).—A method is described for the determination of the dielectric constants of solid and liquid substances by the use of triode valve circuits. The results, with a frequency of $4 \cdot 7 \times 10^5$ per second, were, at the absolute temperatures indicated, as follows: methyl formate, 2·56 at 78·65°; ethyl formate, 2·40 at 81·3°; *n*-propyl formate, 2·39 at 79·5°; *n*-butyl formate, 2·43 at 78·7°; methyl acetate, 2·58 at 77·3°; ethyl acetate, 2·48 at 79·15°; *n*-propyl acetate, 2·42 at 80·9°; *n*-butyl acetate, 2·41 at 77·6°. The values are smaller than those found at the ordinary temperature (5 to 9). The acid radicle apparently contributes but little to the value of the dielectric constant. The dielectric constant of *n*-butyl acetate increases linearly with decrease of temperature to the melting point, at which there is a sudden fall, followed by a very gradual rise as the temperature is still further lowered. J. R. P.

**Conductivity of Concentrated Solutions of Sodium and Potassium in Liquid Ammonia.** CHARLES A. KRAUS and WALTER W. LUCASSE (*J. Amer. Chem. Soc.*, 1921, **43**, 2529—2539).—The specific conductivity of solutions of sodium and potassium in liquid ammonia at its boiling point (−33·5°) has been measured for concentrations from 0·6*N* to saturated solutions. It is shown that as the concentration increases, the specific conductivity increases enormously, reaching the values $0 \cdot 5047 \times 10^4$ and $0 \cdot 4569 \times 10^4$ for saturated solutions of sodium and potassium respectively. The specific conductivity of solutions of sodium and potassium at the same equivalent concentration is very nearly the same. The equivalent conductivity of saturated solutions of sodium and potassium in liquid ammonia is of the same order of magnitude as that of such metals as strontium and iron. The solubility of sodium and potassium in liquid ammonia at its boiling point has been found to be 5·367 and 4·866 mols. of ammonia per atom of sodium and potassium respectively. The general result of the work is the furnishing of further evidence in support of the hypothesis that the conduction process in metals consists in a motion of negative carriers of sub-atomic dimensions, which carriers are identical for all metals. J. F. S.

**Potentials at the Junctions of Univalent Chloride Solutions.** DUNCAN A. MACINNES and YU LIANG YEH (*J. Amer. Chem. Soc.*, 1921, **43**, 2563—2573).—Using a slightly modified form of Lamb and Larson's flowing junction apparatus (A., 1920, ii, 347) the contact potentials of the type, MCl|M′Cl, in which M and M′ are either hydrogen or an alkali metal (lithium, sodium, potassium, cæsium, or ammonium) have been determined. The measurements were made at 25° and were for solutions of equal concentrations

'ables of results of all possible combinations are given for the ɔncentrations 0·1$N$ and 0·01$N$, and the values compared with ıose calculated by Lewis and Sargent's formula (A., 1909, ii, 369). n all cases reproducible values were obtained, within a few undredths of a millivolt. The Lewis and Sargent form of Planck's riginal equation $E_e = RT/F \log_e \Lambda_c/\Lambda_c'$ expresses the results for ıost of the cases studied and gives a qualitative agreement in all ases. The experimentally determined potentials can, however, e obtained from the differences between numbers which are haracteristic for each ion at each concentration. This is equivalent ɔ the expression given above, except that for the lithium and otassium ions, values of $\Lambda$ which are slightly different from those btained from conductivity measurements would have to be used.

J. F. S.

**A Quick Acting Hydrogen Electrode.** P. J. MOLONEY (*J. 'hysical Chem.*, 1921, **25**, 758—761).—A new form of hydrogen lectrode is described. The electrode consists of a short length f platinum wire sealed into the end of a glass tube and projecting mm. from the end; the tube should have an internal diameter f about 4 mm. A loop of 1 mm. diameter glass rod is sealed to he end of the tube so that the platinum wire occupies the centre f the loop. A glass tube, of slightly greater diameter than the lectrode tube, blown into the form of a bell at one end and having bulb a little higher up which is pierced near the top by a small ole, fits over the electrode tube and is kept in position by a piece f rubber tube. The platinum wire is platinised in the usual way. 'he object of the electrode is to ensure a rapid equilibrium between he hydrogen in the platinum and the hydrogen ion in the solu- ion. To use the electrode it is drawn up the tube until the wire nd glass loop are in the middle of the bulb in the jacket tube and he whole is immersed in the liquid to be measured until the tube onnecting the bell and bulb is filled, then the electrode is pushed own until the wire and loop are in the bell, hydrogen is admitted nder the bell, and the whole adjusted so that the wire is sur- ɔunded by hydrogen whilst the lower end of the loop just dips ıto the main bulk of the liquid. In this way only a small volume f liquid, namely, that held in the loop, has to be saturated with ydrogen and be in equilibrium with the wire. Equilibrium values re rapidly reached with this electrode. J. F. S.

**Behaviour of a Non-attackable Electrode in the Process ɩeading to the Equilibrium $3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$.** ɩLFONS KLEMENC (*Z. Elektrochem.*, 1922, **28**, 55, 56); H. PICK *'bid.*, 56—57).—Polemical; cf. A., 1920, ii, 409; 1921, ii, 297.

J. F. S.

**Overvoltage on Electrodes and its Connexion with the ɩydration of Ions.** N. ISGARISCHEV and SOPHIE BERKMANN *Z. Elektrochem.*, 1922, **28**, 40—47).—The decomposition voltage f $N$- and $N$/10-solutions of sulphuric acid and the sulphates of ubidium, aluminium, potassium, ammonium, sodium, lithium,

magnesium, zinc, copper, manganese, and nickel has been determined and the values have been compared with the degree of dissociation, the surface tension, the molecular hydration and the ionic hydration. It is shown that there is only one break in the anode current-voltage curve, and this is attributed to the discharge of the $SO_4''$ ion. The results show that the surface tension is in no way related to the discharge potential of the anion (*E*); the degree of dissociation also stands in no direct relationship to the value of *E*; in some cases it is found that an increase in the value of the degree of dissociation is accompanied by an increase of *E*. It is concluded, therefore, that the discharge voltage is dependent on the velocity of the anode process, that is, a lower potential will be required for decomposition the greater the velocity of the anode process. To investigate the cause of the difference in the velocity of the anode process in different cases, the authors have compared the value of *E* with the hydration of the molecules and the ions. It is shown that there is no connexion between the value of *E* and the number of molecules of water combined with the molecules of the electrolyte. The more hydrated the kations the smaller is the decomposition voltage found to be, and since the more hydrated the kation the less hydrated is the anion, it follows that the lower is the potential required to discharge it. The anode process is expressed by the scheme, (*a*) $SO_4''+2\oplus=SO_4$; (*b*) $SO_4=SO_3+O$; (*c*) $Na_2SO_4(H_2O)_r \rightleftharpoons 2Na(H_2O)_{66}+SO_4''(H_2O)_m$; (*d*) $SO_4''(H_2O)_m \rightleftharpoons SO_4''+mH_2O$. The cause, therefore, of the retardation of the anode process is the insufficiently rapid formation of $SO_4''$ ions from the hydrate. It is shown that there is a definite periodicity between the value of *E* and the atomic weight of the kation.

J. F. S.

**Influence of Colloids on Overvoltage.** N. Isgarischev and Sophie Berkmann (*Z. Elektrochem.*, 1922, **28**, 47—50).—The discharge potential of the hydrogen ion on copper, silver, and platinum cathodes has been measured in 2*N*-sulphuric acid containing various concentrations of gelatin (0—6%). It is shown that the nature of the cathode has no influence on the discharge potential. The value of this quantity at 18° rises to a maximum with increase in the gelatin concentration and then commences to fall. There is a corresponding increase in the anode discharge voltage with increase in the gelatin concentration. The change is explained as due to the formation of a complex between the hydrogen ion and the gelatin which is slowly decomposed at the electrode (see preceding abstract). The maximum potential represents the point where all the ions have combined with gelatin and a calculation based on an approximate value of the molecular weight of gelatin shows that a complex consisting of one hydrogen ion and 1173 molecules of gelatin is formed. J. F. S.

**Free Energy of Dilution and the Activities of the Ions of Potassium Bromide in Aqueous Solutions.** J. N. Pearce and Harry B. Hart (*J. Amer. Chem. Soc.*, 1921, **43**, 2483—2492).—Measurements of the *E.M.F.* of cells of the type Ag|AgBr,KBr(*c*)|

$KHg_x$ have been made for various concentrations ($c=2{\cdot}0$—$0{\cdot}001N$) at 25°, 30°, and 35°. The decrease of free energy and the decrease in heat content attending the reaction in these cells have been calculated. The free energy decrease accompanying the transfer of 1 mol. of potassium bromide from various concentrations ($c$) to $0{\cdot}10N$ have also been calculated. The *E.M.F.* of concentration cells with ion transference of the type $Ag|AgBr,KBr(c_1)|KBr(c_2),AgBr|Ag$ and of concentration cells without ion transference of the types $Ag|AgBr,KBr(c_1)|KHg_x$—$Hg_xK|KBr(c_2),AgBr|Ag$ and $KHg_x|KBr(c_1),AgBr|Ag$—$Ag|AgBr,KBr(c_2)|Hg_xK$ have been determined and from these values the transport number of the potassium ion has been calculated. The results show that dilution has very little influence on the transport number of potassium and there is only a very gradual increase with increasing dilution, whilst the effect of temperature is practically negligible between 25° and 35°. The decrease of free energy and heat content accompanying the transference of 1 mol. of potassium bromide from a concentration $c_1$ to a concentration $c_2$ have been calculated. The activity coefficients of the bromide ion have been calculated and a comparison made of the activity coefficients of the chloride and bromide ions. For all concentrations up to $0{\cdot}5N$, the activity coefficients of these two ions are practically equal. J. F. S.

**Electro-chemical Behaviour of Metallic Conducting Compounds.** G. TAMMANN (*Z. Elektrochem.*, 1922, **28**, 36—40).—A discussion on the electromotive behaviour of compounds which exhibit a metallic conductivity. It is shown that of the five cobalt silicides, only those are attacked by acids which contain more than one atom of cobalt to one atom of silicon. In the case of the lead palladium intermetallic compounds, it is found that they have the palladium potential, but if there is an excess of lead over that required for the formation of a compound in the lead palladium alloy the mixture shows the lead potential. A number of other cases are cited and discussed. J. F. S.

**Activity Coefficients and Colligative Properties of Electrolytes.** HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1922, **44**, 252—267).—A theoretical paper in which on the basis of the empirical equation $\log F_a'=\alpha'c-\beta'c^{m'}$ (A., 1920, ii, 664) which connects the activity coefficient of an electrolyte with the molecular concentration at a given temperature, and Duhem's equation, equations are derived for calculating the vapour pressures of solutions at this temperature. The validity of the above equation has been rigorously tested, and it is found to hold for all electrolytes over the whole range where data were examined with the exception of sulphuric and hydrochloric acids. In these cases, it holds up to a concentration $3M$. The activity coefficients of solutions of hydrochloric acid, sodium chloride, and potassium chloride have been investigated and the values of the parameters of the above equation for these electrolytes and others have been collected and tabulated, from which the vapour pressures and osmotic pressures of their solutions may be calculated. It is suggested that the

equation and method employed here, although empirical and an approximation, will prove useful in testing the consistency and accuracy of activity data and also will be of service in organising the colligative data of concentrated solutions. J. F. S.

**Ghosh's Theory of Electrolytic Solutions.** Charles A. Kraus (*J. Amer. Chem. Soc.*, 1921, **43**, 2514—2528).—A theoretical paper in which the hypothesis of electrolytic solutions put forward by Ghosh (T., 1918, **113**, 449, 627, 777, 790) is discussed. Ghosh's equation expressing the conductivity of solutions of electrolytes as a function of the concentration is compared with the experimental values in aqueous and non-aqueous solutions. On plotting the values of log $A$ against those of the cube root of the concentration, the experimental points lie on a curve which is concave toward the axis of concentration. If Ghosh's equation were applicable, the points should lie on a straight line. The deviation of the points from a linear relation is consistent throughout, and cannot be accounted for by errors in the original observations. It is held that in its present form Ghosh's hypothesis does not satisfactorily account for the properties of solutions of electrolytes. The postulates and assumptions on which the hypothesis is based are discussed and several inconsistencies indicated. The use of Maxwell's law for the distribution of velocities and Clausius's virial theorem to systems of charged particles is open to serious objections. J. F. S.

**Distribution of Thermal Energy in the Quadrivalent Chlorides of Carbon, Silicon, Titanium, and Tin.** Wendell M. Latimer (*J. Amer. Chem. Soc.*, 1922, **44**, 90—97).—The specific heats of carbon, silicon, titanium, and tin tetrachlorides have been measured from the temperature of liquid air to 298° Abs., and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures down to 39·1° Abs., in order to determine the whole specific heat curve for these compounds. The following values of $C_pM/5$ are recorded: Carbon tetrachloride, solid I, 39·1°, 0·60; 40·7°, 0·65; 63·8°, 2·05; 79·6°, 2·81; 91·0°, 3·40; 99·5°, 3·60; 199·5°, 5·84; 208·0°, 5·90; solid II, 229·4°, 6·20; 235·6°, 6·25; 238·0°, 6·77; liquid, 253·8°, 6·40; 265·1°, 6·30; and 290°, 6·34. Silicon tetrachloride, solid, 77·4°, 3·60; 86·6°, 3·83; 94·8°, 4·14; 131·3°, 4·80; 168·6°, 5·68; 181·0°, 5·95; liquid, 208·8°, 6·74; 294·3°, 6·94. Titanium tetrachloride, solid, 86·7°, 4·26; 92·8°, 4·40; 194·6°, 6·19; 231·8°, 6·31; 247·7°, 6·21; liquid, 251·6°, 7·26; 294·3°, 7·32. Tin tetrachloride, solid, 89·0°, 4·59; 95·9°, 4·71; 161·2°, 5·89; 200·7°, 6·33; 227·3°, 6·62; liquid, 266·1°, 756; 294·0°, 7·86. All temperatures are in absolute degrees. The heat of transition of solid I to solid II in the case of carbon tetrachloride at 224·6° Abs. is 7·10—7·19 cal./gram. The heat of fusion has been determined as follows: carbon tetrachloride, [illegible]·1—4·22 cal./gram at 249°; silicon tetrachloride, 10·85 cal./gram 203·3°; titanium tetrachloride, 11·77 cal./gram at 248·0°, and tetrachloride 8·38—8·42 cal./gram at 239·9°. The entropy, each of the compounds at 298° Abs. and the entropy change

*in the formation,* $\Delta S_{298}$, *of each compound from its elements* have been calculated. The following values are recorded: carbon tetrachloride, $S_{298}$, 49·06, $\Delta S_{298}$, −50·84; silicon tetrachloride, $S_{298}$, 56·43, $\Delta S_{298}$, −48·27; titanium tetrachloride, $S_{298}$, 59·51, $\Delta S_{298}$, −47·09; tin tetrachloride, $S_{298}$, 61·84, $\Delta S_{298}$, −49·66.

J. F. S.

**Relation between Statistical Mechanics and Thermodynamics.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 75—90).—A theoretical paper in which the relationship between statistical mechanics and thermodynamics is investigated by a method which is based, like that of Boltzmann and Planck, on a consideration of the arrangement of the elements or molecules of a system. Instead, however, of arbitrarily defining entropy by the equation $S=k \log W$ as do Planck and Boltzmann, an attempt is made to discover a statistical mechanical quantity which has the same derivatives with respect to energy, volume, and number of molecules as does the thermodynamic quantity entropy. In this way, an expression for entropy is developed which differs from that of Planck by an additive term; it is further shown that the addition of such a term is necessary in order that the derivative of the entropy of the system with respect to number of molecules shall have its correct value. The equation thus developed has the form $S=(N\epsilon-N\psi)/T$, in which $N$ is the number of molecules, $\epsilon$ has a significance defined below, and $T$ is the temperature. In connexion with the derivation of the above expression, it is shown that the quantity $\epsilon$ occurring in the Maxwell-Boltzmann distribution law $dN=Ce^{-\epsilon/kT}\, dq_1 \ldots dp_n$ must be taken, not as the energy of a molecule having co-ordinates and momenta falling in the region $dq_1 \ldots dp_n$, but rather as the rate of increase in the total energy of the system per molecule added in the region $dq_1 \ldots dp_n$, when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases, but for concentrated systems may be quite different. Hence the new methods introduced may be of considerable importance in dealing with the properties of imperfect gas or rather concentrated systems. It is pointed out that the equations developed which connect the statistical mechanical quantities with thermodynamic quantities do not agree with the equations of Marcelin and Adams (A., 1915, ii, 328; 1921, ii, 628).

J. F. S.

**Relation between Entropy and Probability. Integration of the Entropy Equation.** GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1922, **44**, 140—142).—Two equations are deduced which express the change of specific heat of an element or compound with the entropy. The equations are based on the assumptions that the change depends on the probability of the "randomness" of the individual particles, the certainty that particles will have a fixed position at the point of zero kinetic energy, and the zero probability that this condition persists at high temperatures. The equations deduced are tested by means of recently published work on the specific heat of copper when a good agreement between the

observed and calculated values of the specific heat over the range 14·51—390·0° Abs. is found. J. F. S.

**Latent Heats of Fusion. I. Benzophenone, Phenol, and Sulphur.** (Mrs.) K. Stratton and J. R. Partington (*Phil. Mag.*, 1922, [vi], **43**, 436—446).—The following values of the latent heats of fusion, in gram-calories per gram, were measured at the melting points by electrical heating: benzophenone, 21·70; phenol, 29·06; sulphur (monoclinic), 8·85. In a theoretical discussion, it is suggested that intramolecular vibrations as well as rotations are indicated in the case of some liquid molecules.

J. R. P.

**The Freezing Points of Pure Organic Liquids as Thermometric Constants at Temperatures below 0°.** Jean Timmermans, (Mlle) H. van der Horst, and H. Kamerlingh Onnes (*Compt. rend.*, 1922, **174**, 365—367).—The following organic liquids have been carefully purified and their boiling points, densities, and freezing points accurately determined, so that these constants may be used as references by working with specimens kept in sealed tubes. All boiling points are given at 760 mm. pressure, and f. p. is the freezing point obtained under conditions where the thermodynamic equilibrium between the liquid and crystalline phases can be maintained for a long time to within 0·01°.

Carbon tetrachloride, b. p. 76·75°; $d_4^0$ 1·63255; f. p. −22·9°; chlorobenzene, b. p. 132·00°; $d_4^0$ 1·12795; f. p. −45·2°; chloroform, b. p. 61·2°; $d_4^0$ 1·52635; f. p. −63·5°; ethyl acetate, b. p. 77·15°; $d_4^0$ 0·92450; f. p. −83·6°; toluene, b. p. 110·70°; $d_4^0$ 0·88445; f. p. −95·1°; carbon disulphide, b. p. 46·25°; $d_4^0$ 1·29270; f. p. −111·6°; ethyl ether (stable form), b. p. 34·60°; $d_4^0$ 0·73625; f. p. −116·3°; (unstable form), f. p. −123·3°; methyl*cyclo*hexane, b. p. 100·3°; $d_4^0$ 0·78640; f. p. −126·4°; *iso*pentane, b. p. 27·95°; $d_4^0$ 0·63950; f. p. −159·6°. W. G.

**Hydration of Ions.** S. Aschkenasi (*Z. Elektrochem.*, 1922, **28**, 58—59).—A theoretical paper in which Fajans's treatment of the hydration of ions (*Naturwiss.*, 1921, 729) is discussed and a possible connexion with the known irregularities in the vapour pressure curves of aqueous solutions of electrolytes suggested.

J. F. S.

**A Receiver for Fractionation in a Current of Gas or under Reduced Pressure.** T. S. Wheeler and E. W. Blair (*J. Soc. Chem. Ind.*, 1922, **41**, 59—60T).—The device consists essentially of an upper and a lower receiver connected together through a two-way tap which makes the connexion alternatively with the top or bottom of the upper receiver. In the former case, the vacuum is maintained in, or the gas is passed through, the upper and lower receivers, whilst the distillate collects in the upper receiver. When it is desired to collect a new fraction, the two-way tap is turned into the second position and the fraction which has collected in the upper receiver passes into the lower one, which is then detached, another put in its place, and evacuated (if neces-

sary), and the distillation continued with the two-way tap in the first position as before. If it is desired to keep the distillate out of contact with air, the lower receiver is provided with inlet and outlet taps, which are turned off before detaching it from the apparatus, and the liquid thus remains enclosed in the inert atmosphere in which it was distilled. G. F. M.

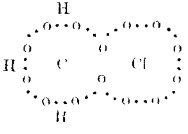
**Comparison of the Linking of Carbon Atoms in Graphite and in Aromatic Hydrocarbons.** J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 96—102).—A theoretical paper based on the work of Fajans (A., 1920, ii, 354), and criticising the theory put forward by von Steiger (A., 1920, ii, 355) that the linking of the carbon atoms in aromatic hydrocarbons is, from the point of view of energy, equivalent to the linking in graphite. H. J. E.

***Atomic Linkings in the Carbon Compounds. I. and II.*** HANS BEUTLER (*Z. anorg. Chem.*, 1921, **120**, 24—30, 31—47).—I. Assumptions that periodic oscillations of melting points and boiling points in homologous series are due to heteropolar linking of the carbon atoms in the chain (cf. Cuy, A., 1921, ii, 429), are shown to be uutenable, on account of the non-dissociation of the carbon compounds. The heats of combustion also vary in an oscillatory manner in homologous series, and this may be explained by considering the lattice-energy of the crystal structure. Compounds with an even number of carbon atoms probably have a more highly symmetrical lattice than those with an odd number, and as a result they have higher melting points and lower heats of combustion. Even in liquids, a kind of potential lattice structure probably exists, and influences the periodically varying physical properties. As the critical temperature is approached, the influence of the lattice is weakened by the strong thermal forces and the differences between odd and even members of the series disappear.

The electron structure of stable ions such as the $Cl'$ or $SO_4''$ ion is discussed, and it is shown that ion formation is due to the splitting of a compound into parts each of which has an electron structure similar to that of a noble gas, with an outer shell of eight electrons. (This is identical with the Lewis-Langmuir theory, to which, however, no reference is made.) The structure of a non-dissociating substance of the type of $Pt(NH_3)_2Cl_2$ is probably such that the co-ordinated groups are attached tetrahedrally to the central atom; in the electron system, the central atom is surrounded by eight electrons forming the corners of a cube, four edges of which are common each to one edge of the electron cubes of one of the co-ordinated groups. The possibility of two isomerides is at once apparent in this arrangement.

II. In the preceding section it was shown that isomerism is possible in the compound of the formula $Pt(NH_3)_2Cl_2$; this is due to the fact that free rotation about the central Pt atom is inhibited probably by directing forces from the inner layers of electrons in the Pt atom. In carbon compounds $CR_1R_1R_2R_2$ free rotation is possible, since only two electrons are contained within the shell of eight electrons and restraining forces are absent. The electron

structures of methane, its halogen substitution products, ethylene acetylene, and aromatic hydrocarbons are discussed. The methane molecule is represented by a central carbon nucleus surrounded by four electrons and four hydrogen nuclei arranged tetrahedrally at the eight corners of a cube with the other four electrons between the carbon and hydrogen nuclei. In $CH_3Cl$ there are fourteen electrons, two of which are common to the eight surrounding the carbon atom and the eight surrounding the chlorine atom. Diagrammatically the electron structure can be represented thus,



where the electrons of the outer shell are represented by small circles. In ethylene it is supposed that the eight electrons which are not situated directly between the hydrogen and carbon nuclei, revolve in an elliptical path of which the major axis is parallel to the C—C axis. The observed paramagnetism attributed to the double bond confirms this view. The electron structural formula for benzene shows three electrons between each pair of adjacent carbon atoms. In naphthalene, three electrons are shown between each pair of adjacent carbon atoms except between the carbons common to both rings, where there are only two. Reduction to 1 : 4-dihydronaphthalene, however, converts one ring into a true benzene ring, and a true ethylenic bond appears between the carbon atoms 2 and 3 in the other ring. E. H. R.

**A Method for Measuring Vapour Densities for the Determination of Atomic Weights.** A. MAGNUS and E. SCHMID (*Z. anorg. Chem.*, 1921, **120**, 232—240).—An apparatus is described for the measurement of vapour densities, the distinguishing feature of which is the total enclosure of the manometer and measuring vessel in a double-walled chamber which can be kept constant at the temperature of boiling water. The apparatus was used for determining the relation between the pressure $p$ and $pv/mT$, where $v$ is the volume, $m$ the weight of the vapour, and $T$ the absolute temperature for benzene and chloroform. Contrary to the results of Ramsay and Steele, the relation was found to be truly linear. The molecular weights calculated from the results are 78·096 for benzene and 119·380 for chloroform, whilst the atomic weight of chlorine calculated from these is 35·455, showing that the apparatus gives results of a high degree of accuracy. E. H. R.

**Regularities in the Molecular Volumes of Inorganic Compounds.** FR. A. HENGLEIN (*Z. anorg. Chem.*, 1921, **120**, 77—84).—It was recently shown by Biltz (A., 1921, ii, 437) that there is a linear relationship between the molecular volumes of the halogens and of their compounds. This is now shown to be a particular case of a more general law that the molecular volumes of certain groups of inorganic compounds of like crystalline form bear a linear relation to constant magnitudes characteristic of their kations or anions. For the halogens, these magnitudes $x$ may be expressed by the constants F′ : 0·8525, Cl′ : 1·000, Br′ : 1·066, I′ : 1·179, and

e magnitudes $y$ for the alkali metals, $Li^{\cdot}$ : 1·000, $Na^{\cdot}$ : 1·428, $^{\cdot}$ : 2·108, $Rb^{\cdot}$ : 2·478. The molecular volumes of the haloids of e alkali metals can be calculated from the general equation ol. vol.$=14·67x \cdot y+0·73x+56·65y-51·60$. Cæsium is abnormal this series, its constant being smaller than that of rubidium though in other series, for example in the sulphates, selenates, anganates, and chlorates, it is normal. The cubic haloids of opper, silver, and thallium form a good series in which the llowing constants appear, $Cu^{\cdot}$ : 1·00, $Ag^{\cdot}$ : 0·920, $Tl^{\cdot}$ : 1·40. Hexa-onal silver iodide does not fit in with the other cubic substances. he same law is shown to hold for numerous other isomorphous ries containing metals of the second and fourth groups. The llowing density determinations were made: lithium fluoride, $^{20·4}$ 2·597; sodium fluoride, $d^{20·2}$ 2·726; potassium fluoride, $d^{18·8}$ ·369. E. H. R.

**The Variation of the Mechanical Properties of Metals and Alloys at Low Temperatures.** LÉON GUILLET and JEAN COURNOT (*Compt. rend.*, 1922, **174**, 384—386).—The hardness and esilience of a number of metals and alloys have been measured t 20°, −20°, −80°, and −190°. The results show that there is, n general, an increase in the hardness with cooling, there being a airly big jump from the value at −80° to that at −190°. Fragility t low temperatures is a characteristic of ferrite, the rapidity of the all in resilience as a function of the temperature being greater as he ferrite content is higher. Nickel and copper, on the other and, do not lead to fragility and aluminium, if present to any great xtent, tends to produce a slight increase in the resilience. Pure ustenite sufficiently rich in nickel does not show fragility at low emperatures. Special perlitic steels containing nickel have a high ragility in liquid air, but the addition of nickel retards the lowering of the fragility with decrease in temperature.

Measurements of hardness and resilience after a specimen has been kept for sixteen hours at −190° and then for twenty-four hours at +20° give evidence of a return to normal properties at the ordinary temperature. W. G.

**Surface Tension of Corresponding States.** RICHARD LORENZ and W. HERZ (*Z. anorg. Chem.*, 1922, **120**, 320—328).—The expression $\gamma_s/\gamma_e=(1-T_s/T_k)/(1-T_e/T_k) \cdot (V_e/V_k)^{2/3}$ is deduced. $T_s/T_k$ and $T_e/T_k$ have been shown by Lorenz (A., 1916, ii, 311) to be practically constant. According to the best average values, $T_s/T_k=0·64$, $T_e/T_k=0·44$, $(V_e/V_s)=0·855$, and therefore $\gamma_s/\gamma_e=0·578$. This was tested on results obtained by Jaeger (A., 1917, ii, 33) and figures are given for 89 organic compounds. The average value for $\gamma_s/\gamma_e$ was found to be 0·52, 75% of compounds agreeing very closely. Twenty-one inorganic compounds of known boiling points gave an average for $\gamma_s/\gamma_e=0·58$. Assuming $\gamma_s/\gamma_e=0·578$, the authors have calculated the boiling points of several salts. The higher the critical temperature the further does $\gamma_s/\gamma_e$ deviate from the mean. W. T.

**Surface Tension of Aqueous Solutions of Night-blue.** R. IZAGUIRRE (*Anal. Fis. Quim.*, 1922, **20**, 40—55; cf. Traube, 1912, ii, 740, 741).—The surface tension of aqueous solutions night-blue of varying concentrations and with the addition different electrolytes was investigated by means of the stalagr meter. The increase of surface tension with concentration is fai rapid at first, but then slows down. In the experiments w addition of electrolytes, it was found that an abrupt fall in surf tension to that for pure water took place at the point where coag ation of the solution occurred. The coagulating power of vari ions can thus be studied by means of the stalagmometer. Ot physical properties, including the aspect under the ultramicrosco do not show this abrupt change at the point of coagulation. Sc tions purified by dialysis give results analogous to those obtai with unpurified material, but the stability of the solutions obtai is less, since smaller concentrations of salts are necessary coagulation. G. W. R

**Theory of Adsorption Processes.** A. EUCKEN (*Z. Elekt chem.*, 1922, **28**, 6—16).—A theoretical paper in which the proc of physical absorption is considered. By physical adsorption understood that adsorption, for example, of argon by charcoal, wh it is unlikely that the adsorbed molecules are held by the attr tions of chemical forces. It is shown that the adsorption for are similar to the forces which are responsible for condensat phenomena. They are practically independent of the temperat and are operative over a relatively small distance which is of same order as the molecular radius. J. F. S

**Adsorption of Ammonia by Silica Gel.** L. Y. DAVIDHEIS and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1922, **44**, 1—8).- continuation of previous work (A., 1920, ii, 417). The adsorpt of ammonia by silica gels containing respectively 4·98% and 0·3 of water has been determined for a series of pressures at 0°, 3 40°, and 100°. A smaller amount of ammonia is adsorbed by less hydrated gel than by the more hydrated compound, althou the less hydrated gel is still capable of adsorbing large amou of ammonia. It is shown that the adsorption of ammonia may satisfactorily explained on the basis of capillary condensati provided corrections are made for the amount of gas which dissol in the water. J. F. S

**Adsorption by Precipitates. V. Adsorption during t Precipitation of Colloids by Mixtures of Electrolytes.** HAR B. WEISER (*J. Physical Chem.*, 1921, **25**, 665—683; cf. A., 19 ii, 269; 1920, ii, 228; 1921, ii, 625).—The precipitation of colloi ferric hydroxide and colloidal arsenious sulphide by the sim taneous addition of pairs of electrolytes, and the adsorption ions during the precipitation of the colloids by mixtures of elect lytes, have been investigated. The precipitation experiments we ried out with pairs of the electrolytes, potassium chlori by

barium chloride, strontium chloride, potassium oxalate, potassium sulphate, and potassium bromate. The adsorption of the oxalate ion in the presence of the chloride and sulphate ion respectively and the barium ion in the presence of the potassium ion was investigated. It is shown that the precipitating action of mixtures of pairs of electrolytes is approximately additive if the precipitating power of each is of the same order of magnitude, but may be far from additive if the electrolytes have widely varying precipitating power. In the latter case, the action of the electrolytes is antagonistic in the sense that relatively more of each is necessary than if the other were absent. In the simultaneous adsorption by solids from mixtures of two electrolytes having no common ion, the most strongly adsorbed kation and anion are taken up most and the other pair least readily; from mixtures having one common ion the oppositely charged ions are each adsorbed less than if the other were absent, but the most readily adsorbed ion is displaced the least. Factors which influence the precipitating action of mixtures of electrolytes are the effect of the presence of each precipitating ion on the adsorption of the other and the stabilising action of the ions with the same charge as the colloid. The second factor is of minor importance with mixtures of electrolytes that have similar precipitation values and have stabilising ions in common. The precipitating action of mixtures of electrolytes with similar precipitating power is additive, since the adsorption of the precipitating ions is similar and consequently the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. With mixtures of electrolytes of widely varying precipitating power, the precipitating action may be approximately additive when the influence of both factors, mentioned above, is small, but may be far from additive when the influence of both factors is large. These extreme cases are realised experimentally. J. F. S.

**Use of the Water Interferometer as a Pressure Gauge.** L. VAN DOREN, H. K. PARKER, and P. LOTZ (*J. Amer. Chem. Soc.*, 1921, **43**, 2497—2501).—The Zeiss water interferometer can be modified so as to serve as a pressure gauge. The modification consists in replacing the two water cells by two brass cells fitted with stout plate glass windows at the ends. One cell is filled with water at atmospheric pressure and the other with water under pressure. On calibrating the instrument, it was found that pressures up to sixty atmospheres could be measured. The range of the instrument may be increased by inserting a thin glass plate in the path of the beam passing through the non-pressure chamber of such a thickness that it will compensate for a pressure of sixty atmospheres in the other chamber. Thus by means of a series of glass plates of different thickness the range of the instrument can be extended to almost any pressure. In the calibration of the instrument for pressures up to 270 atmospheres at 20° and 30° it is found that at the higher temperature the effect of increased pressure on the refractive index diminishes. J. F. S.

**Osmotic Pressures of Concentrated Solutions of Sucrose as Determined by the Water Interferometer.** PAUL LOTZ and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1921, **43**, 2501—2507).—The authors describe a modification of the method used by Frazer and Myrick for measuring the osmotic pressure (A., 1916, ii, 603). The principal feature of the new apparatus is the use of the water interferometer (preceding abstract) for determining the magnitude of the pressures developed. The apparatus is a decided improvement on that of Frazer and Myrick, being more rapid in action and more trustworthy. Pressures up to 273 atmospheres have been measured, but the instrument has been calibrated up to 330 atmospheres. Pressure measurements are recorded for sucrose solutions of concentrations up to saturated solutions at 30° and 55·7°. Attention is directed to the results of Woods as calculated for vapour-pressure measurements, and it is shown that his results (*Trans. Faraday Soc.*, 1915, **11**, 29) showing a decrease in osmotic pressure with rise in temperature in concentrated solutions are relatively correct, although his actual values for the osmotic pressure appear to be high when compared with these direct measurements. J. F. S.

**System: Ammonia–Water as a Basis for a Theory of the Solution of Gases in Liquids.** BENJAMIN S. NEUHAUSEN and W. A. PATRICK (*J. Physical Chem.*, 1921, **25**, 693—720).—A static method has been developed for measuring the partial pressure of a component of a liquid mixture which has a very small partial pressure compared with that of the second component. This method has been used to determine the partial pressures of water and ammonia solutions at 0°, 20°, and 40° at partial pressures of ammonia varying from 1000 mm. to 4000 mm. The measurements in the case of ammonia are made to 2—4 mm., and in the case of water to 0·08 mm. The solubility of ammonia in water was determined at 0°, 20°, and 40° at pressures from 750 mm. to 3600 mm. and the densities of the saturated solutions were also measured. A theory of the nature of solutions of gases in liquids first advanced by Graham has been amplified, and solutions of various gases in liquids classified on the basis of some of the physical and chemical properties of the gas. The formula $V = K(P\sigma/P_0)^{1/n}$ has been found to represent the solubility of ammonia, hydrogen chloride, sulphur dioxide, and carbon dioxide in water at various temperatures and pressures. In this formula $V$ is the volume occupied by the liquefied gas dissolved per gram of water, $P_0$ is the vapour pressure, and $\sigma$ the surface tension of the liquefied gas at the temperature, whilst $P$ is the equilibrium gas pressure. The constant $K$ for ammonia has value 0·49 and $1/n$ the value 0·69. The solubility data of hydrogen chloride, sulphur dioxide, and carbon dioxide have been plotted according to this formula. J. F. S.

**Change of State of Aggregation and Polymorphism.** KARL SCHAUM (*Z. anorg. Chem.*, 1921, **120**, 241—260).—The assumption of Ostwald that there is a relatively broad region of metastability below the normal melting point, in which spontaneous crystallisation

is impossible, appears unnecessary. On the other hand, it is highly improbable that, in a small quantity of liquid in a limited time, the necessary number of molecules in the correct space-lattice orientation to form a nucleus in equilibrium with the liquid at a given temperature will ever come together. It is reasonable to assume with Ostwald the existence of "anisotropic" molecules, but these cannot alone have a "resonance" effect on other "isotropic" molecules and so cause crystallisation. The ageing of a liquid by keeping it some time above its melting point, whereby the tendency to supercooling is increased, is doubtless due to the change of anisotropic molecules into the isotropic form. Anisotropic molecules probably become associated with one another to form space-lattice fragments, and when a crowd of these come together they may cause a field of force strong enough to bring about the formation of a crystal nucleus. As the temperature falls, this process is facilitated through the slowing down of translatory and rotatory motion, but, on the other hand, the probability of the crowding together of anisotropic molecules and space-lattice fragments is lessened.

[With Elli Riffert.]—The crystallisation process is investigated statistically by counting the number of nuclei formed when a thin film of liquid is allowed to crystallise between microscope slide and cover-glass under different conditions. A large number of organic substances were used for the purpose. There is a strong tendency for the nuclei to form in the outer zone of the cover-glass, particularly at the edge, and sometimes they will form again and again at a particular spot. The tendency to nuclei formation at boundary surfaces, especially a triple boundary such as air–glass–liquid, is probably a surface tension phenomenon. The number of nuclei formed increases as the temperature is lowered, finally reaching a maximum. In these experiments, the melted substance was brought suddenly down to the temperature at which the nuclei were to be formed. Pressure may cause the development of nuclei. The substances examined (about 200) fall into five different types, according to the manner in which they crystallise; the states of aggregation assumed by crystallisation from nuclei are described as radiating, bunching, star-like, tabular, and mosaic. E. H. R.

**The $K_\alpha$ Doublet, with New Determinations of the Lattice Constants of some Crystals.** Walther Gerlach (*Physikal. Z.*, 1922, **23**, 114—120).—When a somewhat coarse powder is used in the Debye-Scherrer method, the $K_\alpha$ lines appear double. A method for the measurement of the fine structure of Röntgen lines is described. The lattice constants, in $10^{-8}$ cm., of the following crystals were determined: silicon (identical, within the limits of error, with "amorphous," graphitoidal, and crystalline silicon): 5·415 ($\pm$0·3%) with copper radiation; 5·410 ($\pm$0·3%) with nickel radiation; regular zinc blende 5·390 ($\pm$0·3%) with copper radiation; calcium fluoride 5·455 ($\pm$0·1%) with copper radiation; 5·478 ($\pm$0·2%) with nickel radiation. The doublet distance $K_{\alpha_2-\alpha_1}$

was determined with an accuracy of about 3% as 3·842 *X*.U. (1 "*X*-Unit" $=10^{-11}$ cm.) for copper, and 3·772 *X*.U. for nickel. Bragg's model for fluorite was confirmed. J. R. P.

**Freezing of Hydrosols.** A. LOTTERMOSER (*Kolloid Z.*, 1922, **30**, 133).—A complaint that Gutbier (this vol., ii, 142) has used the author's statements in connexion with the influence of freezing on sols in a manner opposite to that which the author has intended. This has arisen because the author's statements have not been understood in the sense demanded by the context. J. F. S.

**Influence of the Concentration of Colloids on their Precipitation by Electrolytes.** HARRY B. WEISER and HENRY O. NICHOLAS (*J. Physical Chem.*, 1921, **25**, 742—757).—The precipitation of colloidal chromic oxide, Prussian blue, ferric oxide, and arsenious sulphide of various concentrations by electrolytes with precipitating ions of different valency has been investigated. With colloidal chromic oxide, Prussian blue, and ferric oxide, the precipitating values of all electrolytes decrease as the concentration of the colloid decreases, irrespective of the valency of the precipitating ion; but the decrease is least marked with electrolytes having univalent precipitating ions. With colloidal arsenious sulphide, the precipitating value of electrolytes with univalent precipitating ions increases as the concentration of the colloid is decreased. The manner in which the precipitation value of an electrolyte varies with the concentration of colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilising ion. If the adsorption of the stabilising ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large, the precipitation value varies almost directly with the concentration of the colloid. This condition may be realised experimentally with electrolytes which have tervalent and quadrivalent ions which precipitate in extremely low concentration. If the adsorption of the stabilising ion of an electrolyte is appreciable, the precipitating value is increased. This effect is more pronounced the greater the dilution of the colloid, since the decreased opportunity both for the collision and the coalescence of particles combines to render the colloid proportionately more stable so that relatively more of the precipitating ion must be added for complete coagulation. The influence of adsorption of the stabilising ion is more marked with electrolytes having univalent precipitating ions which precipitate only in very high concentration. Under these conditions, the precipitation value decreases much less sharply than under the conditions obtaining when the stabilising ion is only slightly adsorbed, and may even increase as the concentration of the colloid is decreased. The laws put forward by Burton and Bishop (A., 1921, ii, 176) in connexion with the variation in the coagulative power of ions with the concentration of the disperse phase are shown to be quite limited in their applicability. The hypothesis of Kruyt and van der Spek (A., 1919, ii, 498) on the nature of the process of coagul-

ion is inadequate, since it fails to take into account the influence the stabilising ions of electrolytes. J. F. S.

**Relation of Anomalous Osmosis to the Swelling of Colloidal aterial.** F. E. Bartell and L. B. Sims (*J. Amer. Chem. Soc.*, 22, **44**, 289—299).—The authors discuss some seven hypotheses it forward previously to account for the swelling of colloids, and id none of them is applicable to all cases of swelling. The lationship of the swelling of gels to the osmotic effects is con- dered, and as a working hypothesis it is assumed that a gel may considered as composed essentially of a framework of membranes id that the hypothesis which accounts for the flow of a liquid rough membranes also accounts to a certain extent for the flow a solution into a cellular gel. The view is held that swelling the result of imbibition together with the operation of effects hich produce anomalous osmosis. It would therefore follow that swelling the tendency for normal osmosis is always operative, lution in the membrane may take place in some instances, forces attraction and repulsion are operative, capillarity plays a part, gative or positive adsorption of solute may have an effect, ectrical effects due to electrical orientation of the system may ter in, and swelling unaccompanied by electrical effects may cur, as with solutions of non-electrolytes with some gels. For e purpose of comparing anomalous osmotic effects with swelling ects, a series of osmotic pressures using parchment membranes id a series of swelling experiments using *Laminaria* have been rried out with solutions of potassium citrate ($0{\cdot}05M$), sodium droxide ($0{\cdot}0001N$), hydrochloric acid ($0{\cdot}0001N$), and aluminium loride ($0{\cdot}05M$). The results show that those solutions which hibit a negative osmotic tendency with parchment produce a elling effect with *Laminaria*, and those which have a positive motic tendency produce a shrinking of the *Laminaria*. A further ries of experiments with solutions of various electrolytes of veral concentrations confirms the foregoing results. In all cases, e osmosis–concentration curves have the exactly opposite form those of the concentration–swelling curves. J. F. S.

**Lecture Experiment. Protective Colloids.** J. Newton iend (*Nature*, 1922, **109**, 341).—It appears to be a general law at protective colloids or organic emulsoids tend to retard the locities of such reactions, whether chemical or physical, as volve a change of state in one or more of the components. camples of such retardation, the rate of which conforms in many ses to the requirements of the adsorption law, are to be found the solution of metals in acids, corrosion in neutral media, lution and precipitation of salts, and replacement of one metal another. An illustration is afforded by the precipitation of ercuric iodide from solutions of mercuric chloride and potassium dide, the unstable yellow form first precipitated ordinarily turning pidly into the more stable red variety. In the presence, however, 1% of gelatin, after a momentary formation of colloidal mercuric dide, a fine, canary-yellow precipitate is produced, and remains

practically unchanged for half an hour or more. The slow chang to the red variety is markedly accelerated by sunlight. A. A. E.

**Pure Aniline and Water Emulsions.** SHANTI SWARUPA BHATNAGAR (*J. Physical Chem.*, 1921, **25**, 735—741).—The rate of coagulation of aniline-water emulsions by potassium chloride sodium chloride and sulphate, barium, strontium, chromium, and aluminium sulphates has been investigated at 46°. The results show that in general the precipitating power of electrolytes is the same as in the case of many sols, tervalent ions being more effective than bivalent ions and these more so than univalent ions. The order of the precipitating efficiency of the kations is given as Al > Cr > Ba > Sr > K > Na. The effect of dilution on the emulsions is to increase the time required for precipitation; thus an emulsion which is normally precipitated in ten minutes by barium chloride requires eighteen minutes seven seconds when diluted by an equal volume of water saturated with aniline, and when again diluted by the same volume of saturated water forty minutes. J. F. S.

**The Detergent Power of Soap Solutions.** R. T. A. MEES (*Chem. Weekblad*, 1922, **19**, 82—85).—The conception of Martin Fischer of a soap solution as a two-phase system is inadequate, since it does not exclude other gels, for example, gelatin solutions. Similarly, the orientation theory of Langmuir and Harkins does not exclude other substances possessing polarity within the molecule. The unique power of soap solutions to stabilise emulsions can be explained by combining the two theories, since only soaps have the necessary polar character within the molecule without at the same time having molecules soluble as such in oil and water. A soap such as sodium palmitate has the reactive sodium ion, which tends to confer solubility in water, opposed within the molecule to the inert, saturated carbon–hydrogen chain, which tends to confer solubility in oily substances. When such a soap is intimately admixed with an oily substance and water, it forms a bounding layer between the particles of each, its molecules being orientated with the sodium ion towards the water, the carbon–hydrogen chain towards the oil, acting as a layer possessing polar solubilities; in such a system, surface tension disappears.

Earthy impurities, such as clays, resemble soaps in stabilising water–oil emulsions, being lyophil towards both; in presence of soap solution, they are adsorbed by the latter in the bounding surfaces between the particles of oily matter and water.

The detergent power of soaps is therefore primarily a chemical property due to the polarity of molecules insoluble as such in oil and water. S. I. L.

**Cellulose Nitrate as an Emulsifying Agent.** HARRY N. HOLMES and DON H. CAMERON (*J. Amer. Chem. Soc.*, 1922, **44**, 66—70).—The use of cellulose nitrate as an emulsifying agent has been studied. It is shown that this substance serves as an excellent emulsifying agent in dispersing water or glycerol throughout

nyl acetate, acetone, or other solvents for the nitrate. Visible ›ncentration films of cellulose nitrate were observed round large rops of water emulsified in amyl acetate–benzene mixtures. An ıcrease in concentration of cellulose nitrate at the acetone–ycerol interface was observed and studied quantitatively. The roperties of an ideal emulsifying film are discussed. J. F. S.

**Chromatic Emulsions.** HARRY N. HOLMES and DON H. AMERON (*J. Amer. Chem. Soc.*, 1922, **44**, 71—74).—Two immiscible liquids can be emulsified with suitable emulsifying agents, ıch as cellulose nitrate, to produce a transparent emulsion when ıe refractive index of the two phases is the same, and when the spersive power ($n_F - n_c$) of the two phases is the same. A ıromatic (*structural colour*) emulsion is produced when the fractive index of both phases is the same and the dispersive ›wer of one phase is much greater than that of the other phase. he greater the difference the more intense the resulting colour. J. F. S.

**Application of Statistics to Chemical Equilibria.** K. F. ERZFELD (*Physikal. Z.*, 1922, **23**, 95—100; cf. A., 1921, ii, 313).—atistical principles have been applied to chemical equilibria, connexion with polymorphic substances and equilibria in gaseous stems at low temperatures and at high temperatures. A reason advanced for the good agreement found between experimental sults and those calculated by the Nernst approximation formula, ıd it is shown to be probable that the conventional chemical nstant is always about 3. J. F. S.

**Equilibrium in Mixtures of Binary Electrolytes.** CHARLES KRAUS (*J. Amer. Chem. Soc.*, 1921, **43**, 2507—2514).—A eoretical paper in which it is shown that the isohydric principle, hen applied to mixtures of electrolytes, leads to a functional lationship of the form $(C_i)^2/C_u = F(\Sigma C_i)$ in which $C_u$ is the contration of the undissociated fraction, $C_i$ the ion concentration, $C_i$ the sum of the concentrations of all the negative and positive ns in the solution, and $F(\Sigma C_i)$ any explicit function of the total n concentration of the solution. As the concentration of the cond electrolyte diminishes, the function $P_i/C_u = F(P_i)$, in which ı is the ion product, reduces, in the limit, to the same form as e function resulting from the isohydric principle. The values the specific conductivity of mixtures of sodium chloride and ydrochloric acid as calculated according to this principle are own to furnish a better agreement with the measured values an are those on the isohydric principle. J. F. S.

**Partition of Chlorine between Water and a Gaseous Phase.** '. S. TITOV (*Nachr. Physik.-chem. Lab. Semsoinsés*, 1917, 102—110; om *Chem. Zentr.*, 1921, iii, 1222).—The partition of chlorine at )° between water and air containing this gas is given by the rmula $(y-1{\cdot}748)^3x^2=(72{\cdot}52)^3$, where $x$ is the volume of chlorine r thousand volumes of air and $y$ is the volume dissolved in the ater under the corresponding partial pressure. For example,

when $x=10$ parts per thousand, $y=74\cdot27$ under a partial pressur of 7·6 mm. G. W. R.

**Nature of Secondary Valency. III. Partition Coefficient in the System Water–Ethyl Ether.** HOMER W. SMITH (*J Physical Chem.*, 1921, **25**, 605—615, 616—627; cf. A., 1921, ii, 31 324).—In the first paper, details are given of the determinatio of the partition coefficient of forty-nine organic acids and fiftee organic bases at 25° in the system water–ethyl ether. The result obtained from a comparative treatment of these partition coefficient in terms of molecular volume are in good agreement with th results obtained previously (*loc. cit.*) in the systems water–xylenc and water–chloroform. The results are discussed in connexio with the principles laid down in previous papers. The secon paper is a supplementary note on the method of correction employe in the earlier papers. Corrected values for the partition of chloro acetic acid in the system water–chloroform and for a number o organic acids and bases in the systems water–ether are given. J. F. S.

**Nature of Secondary Valency. IV. Partition Coefficient in the System Glycerol–Acetone.** HOMER W. SMITH (*J Physical Chem.*, 1921, **25**, 721—734; cf. preceding abstract).— The partition coefficients of fifty acids, amines, and amin acid phthalates have been determined in the system acetone–glycerol. The present results are in excellent agreement wit those obtained in the systems previously investigated (*loc. cit.*) In the present series of experiments, a fact, which has no been observed previously, is noted, namely, that under certai conditions, concerning the nature of the solvents and the solutes a solute is not distributed, but is concentrated entirely in one o other of the solvents. The series constants for the acids an amines have the same absolute value in this system, as contraste with the different values found in systems containing water a one solvent. Of the substances examined in the system glycerol–acetone, benzilic acid, benzoic acid, αβ-dibromopropionic acid 2 : 4-dinitrobenzoic acid, di*iso*butylamine, salicylic acid, 2 : 4 : 6-trinitrobenzoic acid, and *n*-valeric acid pass completely into th acetone layer. J. F. S.

**Equilibrium in the Reaction between Sulphur Dioxide and Water.** F. RUSSELL BICHOWSKY (*J. Amer. Chem. Soc.*, 1922, **44**, 116—132).—The reactions between liquid sulphur and aqueous sulphuric acid have been investigated over a wide range of conditions. At low concentrations of sulphuric acid, two reactions occur simultaneously, namely, (1) $S_{(\lambda\mu)}+2H_2SO_4(aq)=2H_2O(liq)+3SO_2(gas)$ and (2) $4S_{(\lambda\mu)}+4H_2O(liq)=3H_2S(gas)+H_2SO_4(aq)$. Both reactions are reversible. In the acids of a greater molecular fraction than 0·05, and at temperatures up to the critical temperature of water, the second reaction becomes negligible. Equilibrium pressures for the first reaction have been measured for acids of molecular fractions ranging from 0·041 to

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363 and at temperatures from 527° Abs. to 613° Abs., using an pparatus of a new type. The vapour pressures of sulphuric cid of various concentrations have been measured. Using these nd other existing data, the free energy for the reaction $S_{(\lambda)}+$ $H_2SO_4(M)=2H_2O$(gas)$+3SO_2$(gas) has been calculated to be 500 cal. at 25° and standard conditions. From the data the ee energy of both aqueous sulphuric acid and sulphur dioxide ay be calculated. A new type of apparatus for measuring quilibrium or vapour pressures of corrosive liquids up to high essures and temperatures is described. This consists of a quartz ibe contained in a mercury-filled steel bomb which communicates ith a pressure gauge. The quartz tube is constructed so that e material is contained in a chamber at the top; this communites through a quartz capillary with a second chamber filled with ercury which is in contact with the mercury in the steel jacket. he upper part of the bomb only is heated. J. F. S.

**Equilibria in the Systems: Carbon Disulphide–Methyl lcohol and Carbon Disulphide–Ethyl Alcohol.** E. C. cKelvy and D. H. Simpson (*J. Amer. Chem. Soc.*, 1922, **44**, )5—115).—The temperature of complete mutual miscibility of ixtures of carbon disulphide with ethyl and methyl alcohols spectively have been determined. The critical solution temrature of the system carbon disulphide–methyl alcohol is 35·7° d the critical concentration is about 85% of carbon disulphide; lid methyl alcohol separates from the layer rich in alcohol at -99·6°. The critical solution temperature of the system carbon isulphide–ethyl alcohol is −24·4° and the critical concentration bout 83% by weight of carbon disulphide. All mixtures freeze t −111·7°. It is shown that the critical solution temperature ffers an extremely sensitive criterion of the purity or changes f purity of either component, provided that the other component either pure or of constant composition. Distillation of carbon isulphide from ceresin is shown to remove the impurities and yield perfectly pure product. J. F. S.

**The Quaternary System: Ammonium Chloride–Sodium ulphate–Ammonium Sulphate–Sodium Chloride–Water.** lbert Cherbury David Rivett (T., 1922, **121**, 379—393).

**Induction Periods in Reactions between Thiosulphate and rsenite or Arsenate. A Useful Clock Reaction.** George hannon Forbes, Howard Wilmot Estill, and Osman James Valker (*J. Amer. Chem. Soc.*, 1922, **44**, 97—102).—The precipitaon of arsenious sulphide from an acidified solution (acetic acid) ontaining sodium thiosulphate and arsenite is preceded by an xceedingly sharp and reproducible induction period. The duration f the induction period is strictly in inverse proportion to the oncentration of thiosulphate and is practically independent of he concentration of the arsenite or the acetic acid. Hydrochloric cid prolongs the induction periods and is much better for experiental demonstration of induction periods, of the relationship

between concentration and reaction velocity, and of the temperature coefficient of the reaction velocity, than the familiar sulphurous acid and iodate reaction. The prolongation of the periods by strong acids, the limiting concentrations yielding precipitates when arsenates are used, and the speed of precipitation were also investigated. J. F. S.

**The Combustion of Complex Gaseous Mixtures.** WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1922, **121**, 363—379).

**Oxidation of Nitric Oxide and its Catalysis.** CHARLES LALOR BURDICK (*J. Amer. Chem. Soc.*, 1922, **44**, 244—251).—The rate of oxidation of nitric oxide by oxygen in the presence of glass, pumice, pumice impregnated with tungstic acid, nickel oxide, cobalt oxide, nickel, cobalt, and manganese dioxide, platinised pumice, platinised asbestos, coke, charcoal, and coconut charcoal, has been investigated at temperatures from 0° to 100°. It is shown that the reaction $2NO+O_2=2NO_2$ is not catalysed by ordinary porous material either impregnated or unimpregnated, but that in the presence of the highly absorptive forms of carbon or charcoal the rate of the reaction may be accelerated as much as five hundred times. The presence of water vapour in the gaseous mixtures greatly decreases the activity of the charcoal catalysts. Increase of temperature above the point at which the aqueous vapour condenses counteracts this effect to some extent. The temperature coefficient of the velocity of reaction for both the catalysed and uncatalysed change is generally negative. In the presence of water vapour the temperature coefficient of the catalysed reaction is apparently positive. This is probably due to the decreased absorption of water by the catalyst at elevated temperatures. J. F. S.

**The Transformation of Ammonia into Carbamide.** C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1922, **174**, 455—457; cf. A., 1921, ii, 33).—In continuation of previous work (*loc. cit.*), the yields of carbamide from ammonium carbamate at the equilibrium point at different temperatures are given. Applying the law of mass action to the system in equilibrium the authors calculate the heat of the reaction to be −6 cal., the experimental value being −7·7. The progress of the reaction with time at different temperatures from 130° to 145° has been studied. The curves indicate that the water formed has an effect on the velocity of the reaction. The effect of certain catalysts such as thorium oxide, aluminium oxide, kaolin, etc., has been examined. The results indicate that whilst they may accelerate the reaction at low temperatures, they are without benefit at about 150°. W. G.

**The Processes $NH_2\cdot CO\cdot ONH_4+H_2O \rightleftharpoons (NH_4)_2CO_3$ and $CO_2+H_2O \rightleftharpoons H_2CO_3$.** CARL FAURHOLT (*Z. anorg. Chem.*, 1921, **120**, 85—102).—Experiments on the velocity of the conversion of ammonium carbamate into carbonate indicated that the reaction proceeded first with liberation of carbon dioxide, and this con-

clusion was confirmed by an investigation of the velocity of the reaction $CO_2+H_2O \rightleftharpoons H_2CO_3$. A new method was devised for estimating the proportion of hydrated carbon dioxide, that is, of carbonic acid, in a solution of the gas. When an aqueous solution of carbon dioxide is added to a large excess of ammonia, the anhydrous carbon dioxide immediately forms carbamate, which is so stable in the concentrated ammonia that there is time to precipitate the carbonate as barium carbonate, filter, wash, and titrate it. By this method the dissociation constant of carbonic acid to $H^{+}+HCO_3^{-}$ was found to be $10^{-4\cdot8}$, against $10^{-3\cdot7}$ to $10^{-4\cdot4}$ found by Thiel and Strohecker (A., 1914, ii, 361). This method was applied to making approximate determinations of the velocity of hydration of carbon dioxide in solutions of sodium hydroxide, sodium carbonate, and mixtures of carbonate and hydrogen carbonate. At 0°, hydration is immediate in sodium hydroxide solution, but in a solution containing $Na_2CO_3 : NaHCO_3$ in the ratio 3 : 4 only 77% of the carbon dioxide added is hydrated in the first eighty seconds. Hydration is thirteen times as rapid at 18° as at 0°. Velocity of hydration is inversely proportional to hydrogen-ion concentration. By strong acids, carbonic acid is immediately dehydrated, but by weak acids much more slowly.

The same method of analysis was used for investigating the decomposition of ammonium carbamate in acid, aqueous, ammoniacal, and alkaline solution. Before analysis, the solutions were made alkaline with $0\cdot1N$ sodium hydroxide to stabilise the carbamate. In aqueous solutions containing ammonia and ammonium chloride, the proportion of carbamate present at equilibrium increases with the concentration of either. The equilibrium constant for the reaction $NH_2\cdot CO\cdot O^{-}+H_2O \rightleftharpoons HCO_3^{-}+NH_3$ at 0° had an average value of about 0·34. By even very weak acids, carbamate is immediately decomposed. On adding alkali again, however, some carbamate is re-formed, since two reactions proceed simultaneously with nearly the same velocity, carbamate being formed from ammonia and carbon dioxide, and carbonate from carbonic acid, which is formed at once by hydration of part of the carbon dioxide by the alkali added.

In a 0·05 mol. solution of carbamate in water at 0°, equilibrium is reached in about a day; in a $0\cdot1N$-ammonia solution, three days are required, in a $0\cdot4N$-ammonia solution, ten days; at 18° the reaction is twenty times as fast. In sodium hydroxide solution, the reaction is much slower, requiring about three days in a $0\cdot1N$-solution and a month in a $1\cdot0N$-solution, at 18°. E. H. R.

**The Velocity of Formation of Barium Peroxide.** NOBUJI ASAKI (*Mem. Coll. Sci. Kyoto*, 1921, **5**, 9—96).—For the investigation of the velocity of formation of barium peroxide from barium oxide and oxygen at high temperatures, 400—625°, a special balance was devised, so constructed that the specimen under examination could be weighed at any time, being suspended from one arm of the balance, which was totally enclosed and operated from outside by means of magnets. A new type of gas washer was also devised.

It consists of a U-tube of glass, one arm being narrow and the other expanded into an elongated bulb. The two arms are bridged by a narrow glass spiral in such a manner that the gases, entering by the narrow arm, bubble through the liquid in the spiral and escape at the top of the wide arm, which acts as a reservoir for the washing liquid. The velocity curves for the formation of barium peroxide were of an unusual form. The greater part of the paper is devoted to a mathematical analysis of these curves, and it is shown that they may be explained on the assumption that the oxide consists of a great number of very small, equal spherical particles which begin to react one after another, the number of spheres becoming active in unit time being proportional to the quantity of peroxide already formed. E. H. R.

**The Influence of Protective Colloids on the Corrosion of Metals and on the Velocity of Chemical and Physical Change.** JOHN ALBERT NEWTON FRIEND and REECE HENRY VALLANCE (T., 1922, **121**, 466—474).

**Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid.** C. N. HINSHELWOOD, H. HARTLEY, and B. TOPLEY (*Proc. Roy. Soc.*, 1922, [*A*], **100**, 575—581).—The thermal decomposition of formic acid has been investigated at 283°, and from the results an hypothesis has been formulated in connexion with the mechanism of the reaction. Sabatier and Mailhe (A., 1911, i, 515) have shown that formic acid may decompose according to the equations (*a*) $H\cdot CO_2H=CO_2+H_2$, (*b*) $H\cdot CO_2H=CO+H_2O$, and (*c*) $2H\cdot CO_2H=H\cdot CHO+CO_2+H_2O$. Assuming that in the decomposition certain molecules are activated, either by collision with other molecules or by the absorption of quanta of radiation, the question arises whether every molecule which possesses the necessary critical energy reacts at once or whether, in addition to possessing this, it must be in a certain phase. Under the conditions of the experiments described, only reactions *a* and *b* come into consideration. If $E_1$ and $E_2$ are the critical energies for the two alternative reactions and $N$ is the total number of molecules, it follows from the kinetic theory that the number of molecules possessing these respective energies are $N_1=N\epsilon^{-E_1/RT}$ and $N_2=N\epsilon^{-E_2/RT}$, taking the system as of two degrees of freedom. Then $N_1/N_2=\epsilon^{-(E_1-E_2)/RT}$, so that if one mode of reaction is associated with a slightly lower critical energy it would predominate very largely if the number of active molecules were the only factor. Actually it is found that although the two alternative modes of decomposition of formic acid proceed with the same velocity, yet the critical increments are so different that one reaction should predominate almost entirely unless a phase restriction is introduced, and an interpretation of the phase factor is suggested for this case, as follows. The critical increments for the two reactions are calculated to $E_{CO}=16000$ cal./mol. and $E_{CO_2}=28000$ cal./mol. The numbers of molecules activated for the two reactions are proportional to $\epsilon^{-28000/RT}$ and $\epsilon^{-16000/RT}$, respectively, that is about $\epsilon^{10}$ molecules should yield carbon monoxide for one yielding the

dioxide, but since the rates of both reactions are identical a phase restriction must govern the reaction yielding the monoxide. If the formic acid molecule is assumed to be adsorbed on the glass surface by the residual affinity of the carbonyl group, then in the case of a sufficiently activated molecule a violent collision between the hydrogen- and hydroxyl-groups may occur, and a molecule of hydrogen be split off. Although the requisite degree of activation may be attained but rarely, nevertheless a high percentage of these collisions in activated molecules may result in this type of decomposition. On the other hand, for water to be eliminated and carbon monoxide left, a high degree of activation is not necessary, possibly since the removal of a hydroxyl group, as a whole, from an organic compound is a much less profound change than the fission of the hydrogen and oxygen, but very few of the activated molecules may decompose, because it is necessary to await the contingency that the forces holding the hydroxyl and hydrogen to the carbon should be weak enough to allow the simultaneous "uncoupling" of the molecule. J. F. S.

**The Replacement of Halogen in 4-Chloro-3-nitrobenzonitrile and in 4-Bromo-3-nitrobenzonitrile. II.** T. J. F. MATTAAR (*Rec. trav. chim.*, 1922, **41**, 103—111; cf. this vol., i, 251; also Conrad, Hecht, and Brückner, A., 1890, **4**, 327, and 1046; A., 1891, 796).—In order to measure the effect of the cyanogen group on the replacement of halogen the velocity of reaction of 1-chloro-2 : 4-dinitrobenzene, 4-chloro-3-nitrobenzonitrile, 1-bromo-2 : 4-dinitrobenzene and 4-bromo-3-nitrobenzonitrile with sodium methoxide, with sodium ethoxide, and with sodium phenoxide in both ethyl alcohol and methyl alcohol solution has been investigated. The following conclusions are drawn: (1) the halogen atom is more active in the substituted dinitrobenzene than in the substituted nitrobenzonitrile, (2) chlorine is more reactive than bromine in corresponding compounds, (3) sodium ethoxide reacts more quickly than sodium methoxide, (4) the reaction in ethyl alcohol takes place about twice as quickly as that in methyl alcohol. H. J. E.

**The Effect of Temperature and the Concentration of Hydrogen Ions on the Rate of Destruction of Antiscorbutic Vitamin (Vitamin-*C*).** V. K. LAMER, H. L. CAMPBELL, and H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 172—181; cf. *ibid.*, 165). —Using the quantitative method previously described (*loc. cit.*), the authors claim to have shown that, under the experimental conditions, the velocity of destruction of vitamin-*C* by heat decreases with the time and in greater degree than would be expected if the reaction followed the unimolecular law, or the square root rule of Schutz. The temperature coefficient is of low order, namely, $Q_{10}(60—80°)=1·23$; $Q_{10}(80—100°)=1·12$. The effect of reducing the hydrogen-ion concentration from $p_H=4·3$ to $p_H=5·2—4·9$ is to increase the destruction during one hour at 100° from 50% to about 58%. When the material was made alkaline, $p_H=10·9—8·3$, the destruction was 61—65%. If re-acidification after heating in

alkaline solution was omitted, there was still further destruction, if the material was allowed to remain alkaline for five days at 10°. The material used as the source of vitamin-*C* was tomato juice.

W. G.

**The Influencing of Catalysts and Specifically Active Catalysts.** E. ABEL (*Ber.*, 1922, **55**, [*B*], 322—323).—A final reply to Rosenmund and Zetzsche (cf. Abel, A., 1921, ii, 542; Rosenmund and Zetzsche, A., 1921, ii, 320, 392, 393; this vol., ii, 41).

H. W.

**The Oxygen–Hydrogen Catalysis by the Platinum Metals and the Contact Potentials in Presence of Aqueous Electrolytes.** K. A. HOFMANN (*Ber.*, 1922, **55**, [*B*], 573—588).—Since previous experiments (A., 1920, ii, 240) were performed with platinised porous earthenware tubes, whilst Willstätter and Waldschmidt (A., 1921, ii, 185) employed platinum black, these investigators are not justified in concluding that their results are incompatible with the views of Hofmann and Zipfel (*loc. cit.*). In the present work, no indication could be discovered of the peroxide-hydride, to which Willstätter and Waldschmidt ascribe the favourable effect of oxygen on the catalytic activity of hydrogen (D.R.-P. 301364, Willstätter and Waldschmidt, *loc. cit.*). The volume of oxygen occluded by platinised earthenware is shown to be so small that any peroxide produced cannot bear any relation to the actual effect of oxygen on catalysis, which is rather due to its influence on the catalyst surface. At the same time, the small amounts of gas adsorbed by porous surfaces render them much more suitable than platinum for determinations of variations of contact potential during catalysis. Measurements of the potential difference between such an electrode and one of platinum in contact with hydrogen at atmospheric pressure show that, whether the electrolyte be 17% sulphuric acid or 4% sodium hydrogen carbonate solution, contacts impregnated with platinum, palladinm, or iridium in contact with a mixture of hydrogen and oxygen are electrically modified in the opposite sense to that of their previous treatment (with one or other of the gases), and the more rapidly this occurs the more rapidly is water-formation catalysed. The activity diminishes on prolonged treatment with hydrogen or, especially in the case of palladium, with oxygen. It is improved by repeated variation of this treatment, by repeated use with the stoicheiometrical mixture of the gases, and by varying galvanic polarisation. Light and moderate temperature changes are much less effective. Hydrogen exerts a greater effect on the catalysis potentials with increased hydrogen-ion concentration of the electrolyte, whilst the reverse is true of oxygen. These results indicate that neither pure hydrogen nor hydrogen–oxygen mixtures produce any special oxidising or reducing compound on the catalyst surface of the kind suggested by Willstätter which determines the potential. Direct instantaneous determinations of the effect on the same electrode potentials of the addition of hydrogen peroxide show that this always acts as a strong oxidising agent, and renders it

highly improbable that any peroxide-hydride could exert a strong reducing influence, apart from the extreme rapidity with which the known peroxides are decomposed by platinum metals. Although it is not improbable that hydrogen peroxide is an intermediate product in the formation of water, its existence is so transient as to elude all attempts to detect it. J. K.

**Atomic Structure.** N. BOHR (*Nature*, 1921, **108**, 208—209; cf. *ibid.*, 1921, **107**, 104, 170).—Further examination of the orbits of the electrons postulated in the previous communication has shown that the conception of the atom there outlined cannot be reconciled with that which assumes the atom to be composed of a number of well-defined spherical shells of electrons moving in sharply separated regions. The electrons in the atom are still regarded as being arranged in groups in such a way that the orbit of every electron within a particular group is characterised by the same total number of quanta. In proceeding outwards from the nucleus, the number of quanta characterising a certain group of orbits is larger by one unit than that of the preceding group. The electrons of certain sub-groups will also penetrate into the region of the orbits of electrons of inner groups, giving rise to group-coupling, which is reflected in the stability of the atom. These considerations are applied to the cases of the iron group and the rare earths. A. A. E.

**A Magnetic Model of Atomic Constitution.** J. K. MARSH and A. W. STEWART (*Nature*, 1921, **109**, 340).—If the central magnetic pole in a tank is maintained at a strength always exactly equal and opposite to the combined powers of a number of floating magnets, and if the number of the latter corresponds with units of atomic weight in various elements, the magnets arrange themselves in two clearly defined and sharply separated groups, termed for convenience the nucleus and ring, respectively. It is a remarkable coincidence that the series of groupings obtained corresponds exactly with Aston's suggestions regarding the atomic structure of a number of elements and isotopes. In the case of boron-11 and carbon, both nuclei contain six magnets arranged in two pairs of concentric triangles, a peculiarity which seems to have some connexion with certain chemical and physical similarities. A. A. E.

**Correlation of Atomic Structure and Spectra.** HAROLD S. KING (*J. Amer. Chem. Soc.*, 1922, **44**, 323—328).—A theoretical paper in which it is shown that Bury's modification (this vol., ii, 43) of Langmuir's hypothesis of the structure of elements is confirmed in addition to the relationship between the atomic diameter and the number of electron shells, also by the relationship between the atomic number and the number of lines in the arc and spark spectra, respectively. J. F. S.

**Motion of Electrons in Atoms.** J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **43**, 593—600).—It is shown that when an electron moving with a velocity of the order of $10^8$ cm. per second collides with a molecule of argon it loses only about

one ten-thousandth of its energy, whereas previous experiments showed that in collision with oxygen, nitrogen, or hydrogen, it loses more than 1% of its energy. The mean free path of an electron moving with these velocities in argon is about ten times that in the other gases at the same pressure. J. R. P.

**Relationship between the Internal Friction and the Chemical Constitution of Gases.** HARRY SCHMIDT (*Z. Elektrochem.*, 1922, **28**, 50—55).—A theoretical paper in which the author has deduced equations by means of which the atomic radius of the elements and the mean cross-section of the simpler molecules may be calculated. Using the formula $r=\sqrt{4k\sqrt{M}/7\pi\eta}$, in which $r$ is the atomic radius, $k$ a constant, $M$ the molecular weight, and $\eta$ the coefficient of viscosity, the following values of the radii have been obtained: oxygen, 1·000; nitrogen, 1·035; hydrogen, 0·752; chlorine, 1·491; sulphur, 1·477; bromine, 1·841; helium, 0·795; neon, 0·946; argon, 1·336; krypton, 1·553; xenon, 1·794. The mean cross-section of a number of simple compound molecules are also calculated and tabulated. J. F. S.

**Atomic Radius and Ionisation Potential.** MEGH NAD SAHA (*Nature*, 1921, **107**, 682—683; cf. Basu, *Phil. Mag.*, 1920, [vi], **40**, 619).—The radius, $a_x$, of an atom (the distance from the nucleus to the outermost electron of the Rutherford-Bohr model) may be calculated from the ionisation potential, $V_x$, of an element $x$, from the equation: $a_x=10^{-8}\times(0\cdot532\times13\cdot56)/V_x$ cm. The atomic radii calculated in this way are smaller than those calculated either from crystal data or from the kinetic theory. The following values, expressed as $a\times10^8$, were obtained, those derived from other methods being placed within brackets: hydrogen, 0·530; helium, 0·28 (1·08); neon, 0·33 (0·65, 1·01); lithium, 1·34 (1·50); sodium, 1·41 (1·77); potassium, 1·67 (2·07); rubidium, 1·73 (2·25); cæsium, 1·86 (2·37); copper, 0·94 (1·37); silver, 0·95 (1·77); gold, 0·83; magnesium, 0·95 (1·42); calcium, 1·18 (1·70); strontium, 1·27 (1·95); barium, 1·39 (2·10); zinc, 0·77 (1·32); cadmium, 0·81 (1·60); mercury, 0·69; thallium, 0·99 (2·25); manganese, 0·98 (1·47). A. A. E.

**New Method of Determining Molecular Diameters by the Electromagnetic Rotation of the Discharge in Gases.** C. E. GUYE and R. RÜDY (*Compt. rend.*, 1922, **174**, 382—384).—By applying the theory of ionisation by shock to the phenomenon of rotation of the electric discharge in gases, the velocity of rotation is given by $V=\epsilon H/12\pi\sigma^2 mM$. Thus with a constant magnetic field and for the same gas, the product of the pressure and the velocity observed must be a constant. A new series of measurements has been made on a number of carefully purified gases. The molecular diameters obtained by this method show a close agreement in value with those deduced from viscosity measurements. Contrary to the general opinion, the observed velocity of rotation is not inversely proportional to the density of the gas,

but to the product of the square of the molecular diameter and the density. W. G.

**Atomic Weights and Frequencies.** A. Reychler (*Bull. Soc. chim. Belg.*, 1922, **31**, 67—72).—Warrington's formula for calculating atomic weights (A., 1915, ii, 160) gives too low a value for elements of the two short series. The author's formula, $A=2N+0\cdot007N^2$, gives better values, but is not applicable to hydrogen and is not very satisfactory for elements of the first short series. Attention is directed to the relation of this formula to the equation $\nu=\gamma\ (N-c)^2$, which expresses frequency of radiation of an element when used as an anticathode. H. J. E.

**Qualities of Valency.** R. M. Caven (*Nature*, 1921, **108**, 210—211).—Polemical. Langmuir's (*ibid.*, 1921, **108**, 101) view that the sodium and chlorine atoms in sodium chloride are not united by a chemical bond is attacked, and criticism offered regarding the postulation of covalency and electrovalency in certain cases. A. A. E.

**A Theoretical Derivation of the Principle of Induced Alternate Polarities.** Arthur Lapworth (T., 1922, **121**, 416—427).

**An Explanation of the Property of Induced Polarity of Atoms and an Interpretation of the Theory of Partial Valencies on an Electronic Basis.** William Ogilvy Kermack and Robert Robinson (T., 1922, **121**, 427—440).

**Friend's Theory of Valency.** J. D. Main Smith (*Chem. News*, 1922, **124**, 84—86).—Friend's theory of valency as extended in a recent paper (T., 1921, **119**, 1040) is subjected to a detailed criticism. In particular, the direct translation of Thomson's physical conception of "ionised" and "non-ionised" valency into chemical terms is criticised, on the ground that residual valency may partake of the properties of both. Friend's criticisms of some aspects of Werner's theory are discussed. E. H. R.

**Space-filling and the Equation of Condition.** J. J. van Laar (*Z. anorg. Chem.*, 1921, **120**, 203—208).—A theoretical discussion of the theory of space-filling numbers in relation to van der Waals's equation. E. H. R.

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## Inorganic Chemistry.

**Active Modifications of Hydrogen and Nitrogen produced by α-Rays.** F. H. Newman (*Phil. Mag.*, 1922, [vi], **43**, 455—462).—The α-rays from polonium were allowed to act on nitrogen at different pressures in the presence of sodium, potassium, sulphur, phosphorus, iodine, magnesium, arsenic, mercury, and an alloy

of sodium and potassium. Some gas was absorbed. Similar experiments with hydrogen gave absorptions with sulphur, phosphorus, and iodine. The absorption was shown to be due, at least in some cases, to the formation of nitrides and hydrides. The chemical activity of the gases is due to active modifications, probably consisting of neutral atoms and triatomic molecules, and not to ions. The α-rays are the only ones effective in the rays from radioactive substances. J. R. P.

**Constitution of Hydrogen Peroxides.** B. Oddo and R. Binaghi (*Gazzetta*, 1921, **51**, ii, 343—348).—*See this vol.*, i, 314.

**Separation of the Isotopes of Chlorine.** J. N. Brönsted and G. Hevesy (*Nature*, 1921, **107**, 619).—When a strong aqueous solution of hydrogen chloride is cooled to $-50^\circ$ and evaporated in a high vacuum, the mixture of water and hydrogen chloride being condensed on a surface cooled with liquid air, the condensed portion of the acid is found to be richer, and the remaining portion poorer, as regards the lighter constituent of chlorine, than ordinary hydrogen chloride. After repeated separations, the two portions were converted into sodium chloride, of which saturated aqueous solutions at 20° had *d* 1·20222 and 1·20235, respectively, corresponding with a difference of 0·024 unit in the atomic weights of the chlorine isotopes, if it is assumed that the latter have equal atomic volumes. Equal quantities of the isotopic sodium chlorides were also treated with a slight excess of silver nitrate solution, and the excess of silver salt accurately estimated. The results indicated a difference in the atomic weight of 0·021 unit.

A. A. E.

**The Separation of Chlorine into Isotopes.** William D. Harkins (*Nature*, 1921, **108**, 209; cf. Harkins and Broeker, *ibid.*, 1920, **105**, 230).—See Harkins and Hayes, this vol., ii, 140.

A. A. E.

**Attempt to Separate the Isotopes of Chlorine.** H. Hartley, A. O. Ponder, E. J. Bowen, and T. R. Merton (*Phil. Mag.*, 1922, [vi], **43**, 430—435).—According to Aston, ordinary chlorine consists essentially of a mixture of three parts of $Cl^{35}$ and one part of $Cl^{37}$, and the molecules should be present in the proportions $Cl^{35}Cl^{35} : Cl^{35}Cl^{37} : Cl^{37}Cl^{37} = 9 : 6 : 1$. If light which has passed through a column of such chlorine enters a mixture of chlorine and hydrogen, the initial reaction should use up the three types of molecules in the proportions $1 : 10^9 : 10^{24}$, and the hydrogen chloride formed should be almost entirely $HCl^{37}$. The gas, after exposure, was treated with mercury to remove unchanged chlorine and the hydrogen chloride, absorbed in water, was converted into sodium chloride. The equivalent of the latter, determined by conversion to silver chloride, showed that no separation had occurred within the limits of experimental error. The circumstances which would prevent a separation of isotopes in the experiment are discussed. J. R. P.

**The Atomic Weight of the Chlorine in an Ancient Mineral, Apatite, from Balme.** (MLLE) ELLEN GLEDITSCH and B. SAMDAHL (*Compt. rend.*, 1922, **174**, 746—748).—The chlorine in a sample of apatite from Balme (cf. Curie, A., 1921, ii, 396) was converted into sodium chloride which was carefully purified without possible contamination by chlorine from other sources. Atomic weight determinations gave the value for chlorine as 35·49 and 35·45. Thus taking into consideration the age and origin of the mineral, it may be concluded that the chlorine at the time of the formation of the minerals of the primary magma contained the two isotopes in the same proportion as it does to-day or that the two isotopes were then formed in constant proportions. W. G.

**The Reaction between Iodine and Sulphurous Acid.** ROBERT MILROY MACAULAY (T., 1922, **121**, 552—556).

**Strength of Hypoiodous Acid.** ADOLF FÜRTH (*Z. Elektrochem.*, 1922, **28**, 57—58).—Making use of the constants $[I'][HIO][H^{\cdot}]/[I_2]=3\times10^{-13}$ (Bray, *Abegg's Handb.*, **4**, 2, 456) and $[I_2][I']/[I_3']=1\cdot3\times10^{-3}$ (Jakowkin, A., 1899, ii, 593) and a series of determinations of the concentration of $I_3$ ions in a sulphuric acid solution of various concentrations of iodine in 0·1*N*-potassium iodide by a colorimetric method, the author has calculated the dissociation constant of hypoiodous acid. The values found lie between $1\cdot8\times10^{-11}$ and $4\cdot4\times10^{-11}$, which are in good agreement with a value $4\cdot8\times10^{-11}$ calculated from experiments of Deventer (*Chem. Weekblad*, 1905, **2**, 135). This value shows that hypoiodous acid is about a thousand times weaker than hypochlorous acid.

J. F. S.

**Preparation and Properties of the Persulphides of Hydrogen.** JAMES H. WALTON and LLEWELLYN B. PARSONS (*J. Amer. Chem. Soc.*, 1921, **43**, 2539—2548).—The preparation and properties of hydrogen disulphide and hydrogen trisulphide are described. The two compounds are prepared together by the action of hydrochloric acid on sodium polysulphide. Other acids decomposed the polysulphide completely into hydrogen sulphide and sulphur. Two kilos. of crystallised sodium sulphide and 300 grams of flowers of sulphur are placed in a 3-litre round-bottomed flask and mixed, 800 c.c. of water are added, and the flask is closed with a Bunsen valve. After all the sodium sulphide has dissolved, the flask is heated on a water-bath for three to four hours with occasional shaking, when the whole of the sulphur dissolves and a clear solution of polysulphide is obtained. The polysulphide solution is run into hydrochloric acid (*d* 1·19) which is cooled to −4° to −10°. The addition is made under the surface of the acid at the rate of 3 litres an hour, the solution being rapidly stirred. After a quantity of polysulphide has been added, a brown scum rises to the surface and decomposes with evolution of hydrogen sulphide. At this point, the addition is stopped and the emulsion allowed to settle when a crude oil separates. The oil is a mixture of the two sulphides and about 400—500 c.c. are obtained from

2 kilos. of polysulphide. The oil is separated and dried with phosphoric oxide. The dried mixture is distilled in a quartz glass apparatus fitted with two receivers in series. The first is cooled by cold water and the second by ice and salt. The distillation is carried out at 20—25 mm. pressure and the flask heated in a glycerol bath at 120°. From two volumes of the freshly prepared mixture 2/3 volume of hydrogen trisulphide is obtained in the first receiver and 1/3 volume of hydrogen disulphide in the second receiver, *whilst a residue of sulphur* dissolved *in the* trisulphide remains in the distilling flask. It is essential that quartz apparatus is used in the distillation, because the alkali in glass decomposes both sulphides very rapidly.

The analysis of the persulphides is effected as follows. A weighed quantity (2—3 grams) is placed in a tared quartz test-tube (75 mm.), corked, and weighed. The tube is almost filled with carbon disulphide and the contents are poured into a tared quartz dish (75 mm. diam.), and the tube washed with carbon disulphide. About 20—30 c.c. of carbon disulphide are sufficient. About *10 c.c. of pure acetone are added to the solution, and the dish is* covered by a watch-glass. After the evolution of hydrogen sulphide has ceased, the cover-glass is rinsed with carbon disulphide and the contents of the dish are allowed to evaporate spontaneously and the residue of rhombic sulphur crystals is dried at 90° and weighed. This method is rapid and accurate.

Hydrogen trisulphide, $H_2S_3$, is a mobile, yellow, oily liquid with an odour similar to that of camphor and sulphur monochloride. Its vapours have an irritating action on the eyes and nose. On cooling strongly, the yellow colour is lost and at the temperature obtained with solid carbon dioxide and ether it is quite colourless. It is soluble in benzene, toluene, chloroform, carbon disulphide, ether, and heptane, and is catalytically decomposed by alcohols, ketones, nitrobenzene, aniline, and pyridine. Hydrogen trisulphide behaves like glass on cooling, becoming more and more viscous as the temperature is reduced to −75°, but on warming again there is a short delay in the rise of temperature at −52° to −53°. It may be distilled in a vacuum, but at atmospheric pressure it foams, evolves hydrogen sulphide, and leaves a gummy residue of sulphur in the mixed sulphides.

*Hydrogen disulphide*, $H_2S_2$, has not been obtained quite free from trisulphide, the amount of impurity is not large and is represented by a deficiency of 1—2% of hydrogen sulphide on decomposition. It is a colourless, mobile oil with a much more severe and irritating odour than the trisulphide, causing tears and a smarting sensation in the nostrils. It is soluble in the same solvents as the trisulphide, but is much more sensitive to impurities. Acetone catalyses the decomposition very violently, so that great care is required in the analysis. It boils at 74·5° and melts between −88° and −90°, but shows no sharp point of solidification.

Hydrogen trisulphide has the same action on solutions of copper [illegible] ferric chloride, stannic iodide, silver nitrate, and mercuric [illegible] in ether as hydrogen sulphide. Silver oxide, cupric

oxide, lead dioxide, and mercuric oxide decompose hydrogen trisulphide so violently and with such development of heat that it is ignited; lead oxide, stannic oxide, and magnetite decompose it violently, whilst arsenious, arsenic, ferric, and zinc oxides, barium dioxide, and manganese dioxide bring about only a slow decomposition. Potassium permanganate and potassium dichromate decompose it violently. Most metallic salts decompose the trisulphide, but massive metals have a very slow action. It dissolves readily in liquid hydrogen sulphide and one molecule of the trisulphide dissolves eight atoms of sulphur. J. F. S.

**Influence of Freezing on Colloidal Selenium. III.** A. GUTBIER and R. EMSLANDER (*Kolloid Z.*, 1922, **30**, 97—110; cf. A., 1921, ii, 693; this vol., ii, 142).—Further experiments on the effect of freezing on selenium sols are described. It is shown that selenium sols prepared by means of hydrazine hydrate are stable toward freezing when of suitable concentration, even in the presence of large concentrations of selenious acid. The stability of such sols is dependent on the temperature of formation to a marked extent. A particularly stable system is formed when a 0·002*M* solution of selenium dioxide is reduced by a 1 : 2000 solution of hydrazine hydrate at 60°, ten parts of selenium dioxide solution being reduced by one part of hydrazine hydrate. The coagulation of selenium sols is greatly accelerated by freezing. Selenium sols may be prepared by the solution of selenium in hydrazine hydrate at ordinary temperature and pouring this molecular disperse system into a large volume of water. With this system, it is shown that the stability of colloidal selenium depends mainly on the degree of dispersion. It is also shown that an optimum concentration of electrolyte is necessary for the stability of selenium hydrosols. In the absence of electrolytes, this system is quite unstable toward freezing. The protective action of the sodium salts of protalbic and lysalbic acids on selenium sols consists in a retardation of the spontaneous coagulation of the suspensoid.

J. F. S.

**Hydrates of Selenium Dioxide.** WILHELM MANCHOT and KARL ORTNER (*Z. anorg. Chem.*, 1922, **120**, 300—309).—Crystallisation of solutions of selenium dioxide did not give trustworthy results, because the crystals obtained were very hygroscopic and could not be dried in a desiccator without undergoing decomposition. The freezing curve of hydrated selenium dioxide showed only one eutectic point at −23°; the eutectic mixture containing 57% $SeO_2$, and consisting of ice and the hydrate $SeO_2,H_2O$. A maximum was found on the solubility curve corresponding with a composition of 86·07% $SeO_2$, that is, $SeO_2,H_2O$. The vapour pressure curve indicated that $SeO_2,H_2O$ was the only hydrate present. Molecular weight was found by the freezing-point method. The degree of dissociation was found to be approximately the same as for tartaric acid. No evidence could be obtained of the existence of the associated selenious acid $(H_2SeO_3)_2$ in a

freshly prepared solution as claimed by Rosenheim and Krause (this vol., ii, 47). W. T.

**The Elimination of the Heat of Reaction in the Synthesis of Ammonia by High Pressures.** GEORGES CLAUDE (*Compt. rend.*, 1922, **174**, 681—683).—The device adopted to remove the heat of reaction consists in having the catalyst in a thin-walled inner tube and allowing the oncoming cold gases to circulate through the annular space. The inner tube is so constructed that the amount of heat removed at any one point is just equal to the heat generated at that point. This is effected by varying the thickness of the inner tube along its length. With this new arrangement it is claimed that the life of the reaction tube is considerably increased and the catalyst can very easily be replaced when necessary. W. G.

**The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia. Influence of Hydrogen Phosphide.** E. DECARRIÈRE (*Compt. rend.*, 1922, **174**, 460—461; cf. A., 1921, ii, 503, 546).—Hydrogen phosphide when present in the ammonia–air mixture as the sole gaseous impurity and only to the extent of 0·00002% exercises a harmful effect and reduces the oxidation by nearly 30%. If the gas is present to the extent of 0·02%, the yield falls from 93·8% to 3·9%. In every case, however, the activity of the catalyst is regenerated when the impurity is removed, the regeneration being slower the greater the percentage of the impurity previously present. In some cases, however, industrial catalysts of the type of those of Ostwald may be destroyed by the momentary presence of traces of hydrogen phosphide in certain favourable circumstances. W. G.

**The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia Gas.** EUGÈNE DECARRIÈRE (*Compt. rend.*, 1922, **174**, 756—758; cf. preceding abstract).—It has previously been shown that hydrogen sulphide is capable of partly neutralising the injurious influence of acetylene in the catalytic oxidation of ammonia in the presence of finely divided platinum. It is now shown that it can also partly neutralise the injurious influence of hydrogen phosphide. This beneficial effect is not due to the dissociation of the sulphide with the consequent liberation of hydrogen, since hydrogen itself is incapable of neutralising the effect of the phosphide. W. G.

**Nitrous Anhydride.** F. FOERSTER (*Ber.*, 1922, **55**, [*B*], 490—491).—In a recent communication (A., 1921, i, 778) Wieland has shown that nitrous fumes behave in many respects as if constituted entirely as nitrous anhydride, $N_2O_3$, and has assumed that, in spite of density determinations, a small proportion of this substance must be present in equilibrium with the mixture of nitric oxide and nitrogen peroxide. The experimental evidence on this point has been provided by Le Blanc (*Z. Elektrochem.*, **1906**, **12**, 544) and the author (A., 1910, ii, 1059). H. W.

**Magneto-chemical Investigation of the Constitutions in Mineral Chemistry. The Acids of Phosphorus.** PAUL PASCAL (*Compt. rend.*, 1922, **174**, 457—460).—The method of magnetic analysis previously applied to the compounds of sulphur (A., 1921, ii, 692) has now been applied to compounds of phosphorus. The molecular susceptibilities of a number of phosphorus compounds are given. In all its incompletely saturated derivatives the diamagnetism of phosphorus or its oxy-groups is greatly weakened, and phosphorus and its oxy-radicles possess a constant magnetic individuality. In its saturated derivatives, phosphorus has a different but constant magnetic susceptibility. The results accord perfectly with the rational formulæ $PO(OH)_3$, and $RPO(OH)_2$ for the phosphoric and phosphinic acids. W. G.

**The Use as a Drying Agent of Phosphoric Oxide Treated with Ozone.** JOHN JOB MANLEY (T., 1922, **121**, 331—337).

**Atomic Weight of Boron.** G. P. BAXTER and A. F. SCOTT (*Science*, 1921, **54**, 524—525).—Boron was obtained by reduction of boric oxide with excess of magnesium, and extraction with either hydrochloric or hydrobromic acid. It was then converted into the haloid by passing over it at 700° either dry chlorine or helium saturated with bromine nearly at the boiling point of the latter. The excess of halogen having been removed, the haloids were repeatedly distilled with the use of Hempel fractionating columns in sealed, all-glass vessels, with the exclusion of air. Analysis was effected by comparison with silver in the usual way, and by each method gave a result of 10·83±0·01. This indicates the proportion of the heavier isotope to be about five times that of the lighter, a result which is more in accord with the observations of Aston (A., 1920, ii, 718) than the previous determination (10·900) by Smith and van Haagen (A., 1920, ii, 247). A. A. E.

**Researches on the Chemistry of Coal. II. The Resinic Constituents and Coking Propensities of Coals.** W. A. BONE, A. R. PEARSON, E. SINKINSON, and W. E. STOCKINGS (*Proc. Roy. Soc.*, 1922, [*A*], **100**, 582—598; cf. *ibid.*, 1917, [*A*], **96**, 119).—Strongly coking bituminous coals may be extracted for prolonged periods by organic resin solvents without impairing their coking propensities. It is shown that the pyridine–chloroform method of extracting coals does not, as stated by Clark and Wheeler (T., 1913, **103**, 1706), effect a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated; but that, on the contrary, it yields an admixture of resins with a predominance of non-resinous substances, which latter are chiefly of cellulosic origin, and have been provisionally designated "humic" substances in the present paper. It is shown that resins may be extracted and isolated in a pure condition from such coals by treatment with pyridine and amyl alcohol, in equal proportions, in an atmosphere of nitrogen, followed by successive treatments with ethyl ether and light petroleum. These resins do not normally much exceed

1% of the coal substance, and, although they may be a contributor are not usually the chief cause of the coking propensities of coal A series of non-resinous substances, amounting in many cases t as much as 4%, may be extracted from strong coking coals by special pyridine or pyridine–amyl alcohol treatment. These sul stances for the most part are insoluble in ether but soluble i chloroform. On heating these substances out of contact wit air, a strong exothermic reaction takes place between 275° an 375° which is accompanied by the elimination of water. Th reaction is reminiscent of the behaviour of cellulose and show these substances to be chiefly cellulosic in type and origin. Th coking propensities of coals are principally due to the presence, c the formation in them by heat, of such non-resinous substances c cellulosic origin, the fusion temperatures of which are below thos at which they undergo rapid decomposition. The still more con plex substances, also of cellulosic origin, which constitute the mai portion of the coal substance, but which decompose without fusion have little or no direct influence on its coking propensities.

J. F. S.

**Modifications of Silicon. Solubility of Silicon in Hydro fluoric Acid.** WILHELM MANCHOT and HERBERT FUNK (*Z anorg. Chem.*, 1922, **120**, 277—299).—Specimens of silicon obtaine from an aluminium regulus have been examined and the influence of (1) temperature of the fusion, (2) concentration of silicon, an (3) rate of cooling investigated. The temperature of the fuse mass was varied from 900° to 1650° and was found to have bu little effect. The concentration of silicon could be varied fro 0·25 to 10% without much effect, but a higher concentratio (>10%) favoured the formation of crystals. Rapid cooling c the regulus gave a greyish-black, amorphous (no crystalline form could be detected at 960 magnification) silicon (*d* 2·23) whic reacted briskly with hydrofluoric acid with evolution of hydroge leaving a brown, amorphous residue (*d* 2·20) apparently insoluble i hydrofluoric acid. This brown variety was found to be ver active—reacting violently with fuming nitric acid, sodium hydr oxide, chlorine, and bromine at ordinary temperatures. Thi reactivity was found to be due to adsorbed hydrogen; after re moving the hydrogen it reacted with hydrofluoric acid and behave in the same way as the greyish-black, amorphous form. O cooling the regulus slowly, crystalline silicon was obtained (*d* 2·30) this form reacted but slowly with hydrofluoric acid. The aluminiu could be replaced by a silver regulus. Silicon of 99% solubility i hydrofluoric acid as claimed by Moissan and Siemens (A., 1904 ii, 560) could not be prepared. Silicon in the mixture (silicon an silica) was estimated by the volume of hydrogen liberated fro potassium hydroxide solution. Silicon completely resistant towar hydrofluoric acid could not be prepared. Ordinary silicon heated a 2000° and suddenly cooled behaves in the same way as when slowl cooled. This leads the author to believe that the various form obtained from the reguli are not allotropic modifications. Th

sudden cooling of the solution and solidification of the metal solvent gives extremely fine particles ($d=1\mu$); the reactivity is ascribed to this fineness and not to a new form. Such a degree of fineness could not be obtained mechanically. W. T.

**Formation of Potassium Perchlorate from Potassium Chlorate.** VICTOR LENHER, HOSMER W. STONE, and HELEN H. SKINNER (*J. Amer. Chem. Soc.*, 1922, **44**, 143—144).—The formation of potassium perchlorate from potassium chlorate by the action of acids has been investigated. On treating potassium chlorate with sulphuric acid, taking care to add the acid slowly and keeping the mixture cold until the yellow colour has disappeared, a yield of 11% of perchlorate is obtained. Evaporation to dryness of chlorate with nitric acid of various concentrations on a steam-bath gives a yield of 30% of perchlorate; fuming nitric acid yields no perchlorate under the same conditions. A 15% yield of perchlorate is obtained when potassium chlorate is boiled with 85% phosphoric acid. Potassium chlorate and chromium trioxide boiled with just sufficient water to maintain a solution give 11% of perchlorate. Chloric acid gives no perchlorate with potassium perchlorate. The following acids have no action of potassium chlorate even at the boiling point: saturated oxalic acid solution, 25% tartaric acid, acetic acid both glacial and dilute, 50% chloroacetic acid, 25% lactic acid, 50% arsenic acid, 20% permanganic and persulphuric acid. Formic, trichloroacetic, hydrofluoric, and hydrochloric acids decompose potassium chlorate without producing perchlorate. J. F. S.

**Preparation and Constitution of a Double Potassium Ammonium Orthophosphate.** R. M. CORELLI (*Gazzetta*, 1921, **51**, ii, 380—385).—Attempts to prepare a salt analogous to sodium ammonium hydrogen orthophosphate by the interaction of dipotassium hydrogen phosphate and ammonium chloride or phosphate result in the elimination of ammonia and formation of potassium dihydrogen phosphate. This extreme instability indicates the compound formed to be a tertiary phosphate, and *potassium diammonium phosphate*, $K(NH_4)_2PO_4,4H_2O$, may be obtained by passing ammonia into aqueous potassium dihydrogen phosphate solution cooled in ice and salt, filtering the solution quickly in an atmosphere of ammonia and pressing the crystals between filter-paper. The compound deliquesces and loses ammonia in the air, but may be preserved in sealed tubes. T. H. P.

**Crystal Structures of Potassium and Ammonium Stannichlorides.** ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 276—288).—The crystal structures of potassium and ammonium stannichlorides have been determined from measurements of the $X$-ray reflection spectra and from unsymmetrical Laue photographs. The structure is shown to be similar for the two salts and of the calcium fluoride type. It has been found possible to carry out the analyses without making any quantitative assumption concerning "normal decline" of intensity, and with only

rough assumptions as to the relative reflecting powers of the atoms. The results lead to the conclusion that six equivalent chlorine atoms are grouped about each tin atom; and the structure is accordingly regarded as built up of $SnCl_6''$ ions and potassium or ammonium ions. The $SnCl_6''$ ion occupies the positions filled by calcium in fluorspar and the potassium or ammonium ions occupy the positions of the fluorine. It is shown that the general structure and cleavage of the crystals investigated are similar to those of fluorspar. The following distances between the atoms are recorded: potassium stannichloride, between tin and chlorine, 2·44 Å.U., tin and potassium, 4·31 Å.U., potassium and chlorine, 3·52 Å.U., ammonium stannichloride, tin and chlorine, 2·46 Å.U., nitrogen and tin, 4·35 Å.U., and nitrogen and chlorine, 3·55 Å.U. J. F. S.

**Simple Method for the Preparation of Sodium Hydroxide Free from Carbon Dioxide.** JACOB CORNOG (*J. Amer. Chem. Soc.*, 1921, **43**, 2573—2574).—Solutions of sodium hydroxide free from carbonate may be prepared as follows. Distilled water contained in an Erlenmeyer flask is boiled to remove carbon dioxide, after which, when the water has cooled sufficiently, a layer of ethyl ether 3—4 cm. deep is placed on the water. Pieces of metallic sodium, not exceeding 1 cm. in diameter, are dropped into the flask. They fall no further than the ether, where they remain suspended and are slowly attacked by the water dissolved in the ether and the sodium hydroxide passes into the water. After the desired quantity of sodium has reacted, the larger portion of the ether is pipetted off and the last traces are removed by boiling the solution. It is shown that there is no danger of fire if the depth of the ether is great enough to prevent the suspended sodium from being simultaneously in contact with the air and water. With the care usually employed in working with ether and by keeping the ether layer from three to four times as thick as the diameter of the pieces of sodium added, the reaction may be performed easily and without danger. A further advantage of using ether is that the oil adhering to the sodium is removed with the ether. The product gives uo precipitate with solutions of barium hydroxide. J. F. S.

**Sodium Hyposulphite.** FREDERICK W. HEYL and FRANK E. GREER (*Amer. J. Pharm.*, 1922, **94**, 80—92).—The most satisfactory laboratory method for the production of sodium hyposulphite is by the action of sodium formaldehydesulphoxylate on sodium hydrogen sulphite. The former substance may be prepared by the method of D.R.-P. 256460, or more conveniently by the reduction of commercial "hydrosulphite" with zinc dust and zinc oxide in presence of formaldehyde solution, and recrystallising from water at a temperature not exceeding 70° the crystals first obtained. The purity of the product, which approximates to 100%, is best determined by direct titration of a hot solution with standard solution of methylene-blue. Sodium formaldehydesulphoxylate is soluble in glycerol to the extent of about 74 grams in

100 c.c. Administered intravenously, it apparently has no toxic action on white rats. It was not found possible to prepare analytically pure anhydrous sodium hyposulphite even by the method from the sulphoxylate indicated above, and salting out the product with strong brine, although a purity of 97·7% is claimed in U.S. Pat. 990457. The yields obtained amounted to 55—60% of the theoretical with a purity of 80—85%, and neither by recrystallisation nor salting out from air-free aqueous solutions in an inert atmosphere could the salt be further purified. Unlike the sulphoxylate, sodium hyposulphite and also its decomposition products are toxic in doses of about 200 mg. upwards per kilo. of body weight.

G. F. M.

**The Density of Cæsium at the Absolute Zero.** W. Herz (*Z. anorg. Chem.*, 1921, **120**, 159).—In a previous paper (A., 1919, ii, 220), it was overlooked that, in calculating the density of a number of elements at the absolute zero, the value arrived at for cæsium, 1·791, is lower than the density at higher temperatures. The equation used cannot therefore be applicable to cæsium. A value harmonising better with that of the other alkali metals is obtained by taking the density at 27° as the density at the melting point $d_e$, and applying the relation $d_0 : d_e = 1{\cdot}21$, when the value 2·222 is obtained, and the corresponding atomic volume 59·77. A correction must be made in a subsequent paper in which the atomic volume at absolute zero is used for calculating molecular volumes of cæsium salts (Lorenz and Herz, A., 1921, ii, 536).

E. H. R.

**Highly Basic Lithium Salts of Weak Inorganic Acids.** Arthur Rosenheim and Werner Reglin (*Z. anorg. Chem.*, 1921, **120**, 103—119).—It has been shown that some highly basic salts of lithium, such as those of antimonic and periodic acids, have semi-colloidal properties (A., 1918, ii, 194 and 1919, ii, 508). Those lithium salts which are characterised by low solubility and negative temperature coefficient of solubility are generally those of weak acids which may be expected to form polymerised or associated molecules. A number of such lithium salts, including phosphite, hypophosphate, phosphate, vanadate, molybdate, tungstate, borate, and carbonate, have been examined with respect to their state of aggregation.

Dilithium hydrogen phosphite, $Li_2HPO_3,H_2O$, has a negative temperature coefficient of solubility in water, which ranges from 9·07 grams at 0° to 4·24 grams at 98° of anhydrous salt per 100 grams of solution, the solid phase being the monohydrate throughout. The hydrogen-ion concentration at 20° in a normal solution is 7·34 . $10^{-9}$ ($P_H = 8{\cdot}14$). The equivalent conductivity at dilutions from $v=32$ to $v=1024$ was measured, and also the freezing-point depression. The values for the latter do not indicate association in solution.

Lithium hypophosphate, $Li_2PO_3,3{\cdot}5H_2O$, does not form a clear, aqueous solution and its solubility would not be determined directly with accuracy. An estimate of the solubility was made from the conductivity, making use of known data to calculate the migration

velocities of the ions. The value obtained for the solubility was 0·1267 gram of $Li_2PO_3$ per litre at 25°, a value much lower than the apparent solubility determined directly. Whether the apparently colloidal solution is really colloidal or a non-colloidal suspension cannot be stated.

Lithium phosphate was obtained in the form of a dihydrate, $Li_3PO_4,2H_2O$, which at 60° is slowly converted into $Li_3PO_4,\frac{1}{2}H_2O$. It also forms a cloudy solution; the solubility, determined by the conductivity method, is 0·297 gram of $Li_3PO_4$ per litre at 25°. Two compounds of lithium with vanadic acid were obtained. The first, $4Li_2O,V_2O_5,4H_2O$, is precipitated when a solution of vanadium pentoxide in a large excess of a saturated solution of lithium hydroxide is heated. It appears to have a negative temperature coefficient of solubility, but at low temperatures when stirred with water it changes into $3Li_2O,V_2O_5,18H_2O$ or $Li_3VO_4,9H_2O$, transparent, rhombohedral needles. This appears to be identical with *Ditte's* $4Li_2O,V_2O_5,14H_2O$ (*A.*, 1887, 705). The solubility coefficient of $Li_3VO_4,9H_2O$ is positive, the maximum solubility being 6·25 gram of $Li_3VO_4$ per 100 grams of solution at 35·2°; above this temperature, the monohydrate is stable and the temperature coefficient is negative.

Lithium molybdenate was found to have the composition $4Li_2MoO_4,3H_2O$, not $5Li_2MoO_4,2H_2O$ (Wempe, A.,. 1913, ii, 59). Its solubility at 25° is 44·81 grams of $Li_2MoO_4$ per 100 grams of solution and the temperature coefficient is small and negative. The tungstate has a similar composition, $4Li_2WO_4,3H_2O$, and its solution is rapidly decomposed by atmospheric carbon dioxide.

Lithium borate, $LiBO_2,8H_2O$, has a positive solubility coefficient and shows normal depression of freezing point in solution.

Lithium carbonate when boiled in aqueous solution loses carbon dioxide, and finally a solution is obtained containing $LiOH : Li_2CO_3 = 1 : 1$ (approx.). It follows that the solubility determinations of Bewad (*J. Russ. Phys. Chem. Soc.*, 1884, **16**, 591) are not trustworthy at higher temperatures. E. H. R.

**Crystallographic and Atomic Symmetries of Ammonium Chloride.** Ralph W. G. Wyckoff (*Amer. J. Sci.*, 1922, [v], **3**, *177—183*).—The symmetry of ammonium chloride as indicated by the development of the external faces and by etch-figures on the faces is that of the enantiomorphous hemihedral class, whilst from the *X*-ray data, both with the spectrometer and the powder method, the internal structure is tetrahedral cubic with one chemical molecule to the unit cell. The latter is based on the ratio $n^3/m=1$, where $n$ is the order of the reflection and $m$ the number of molecules in the unit cell. Several more complex enantiomorphous groupings with several molecules in the unit cell are considered; but from a chemical point of view these are highly improbable, since they collected all the ammonium groups about one point in the unit and all the chlorine atoms about another point. The crystallographic observations are therefore regarded as requiring revision. L. J. S.

**Decomposition and Stabilisation of Ammonium Nitrate in Presence of Oxidisable Material.** ALEXANDER FINDLAY and CYRIL ROSEBOURNE (*J. Soc. Chem. Ind.*, 1922, **41**, 58—59T).—The stability of mixtures of ammonium nitrate with small quantities of woodmeal and with starch was investigated by heating the mixture contained in a test-tube, provided with a capillary delivery tube leading below the surface of mercury to a graduated gas burette. The tube was exhausted and placed in a boiling water-bath. A mixture of 23·75 grams of ammonium nitrate and 1·25 grams of woodmeal gave 1·5 c.c. of a mixture of carbon dioxide (33·1%) and nitrogen (66·9%) in twenty-four hours, and 47·1 c.c. in fifty days. A mixture of the same amount of nitrate and 2 grams of soluble starch gave in one day 46·5 c.c. of a gas having the composition $CO_2$ 27·04%, $N_2$ 72·4%, and CO 0·56%. After some days, the rate of evolution slowed down considerably, and eventually the gas evolved appeared to consist of nitrogen only. In both cases, the addition of 0·25 gram of carbamide to the mixtures proved a most effective stabiliser, no appreciable evolution of gas occurring with the woodmeal mixture in a period of thirty-five days. Diphenylamine and phenyl benzyl ether also act as stabilisers, but they are not suitable for the purpose, owing to subsidiary reactions occurring between these substances and the ammonium nitrate. G. F. M.

**Solubility of Silver Chloride in Dilute Chloride Solutions and the Existence of Complex Argentichloride Ions. II.** GEORGE SHANNON FORBES and HARRIET ISABELLE COLE (*J. Amer. Chem. Soc.*, 1921, **43**, 2492—2497; cf. A., 1912, ii, 49).—To solutions of sodium, ammonium, hydrogen, rubidium, calcium, barium, strontium, and potassium chloride of concentrations not greater than 0·1*N* a 0·001*N*-solution of silver chloride was added at 25° until an incipient precipitation was observed. The total silver then in solution was invariably given by $2\times10^{-10}/(MCl)+3\cdot4\times10^{-5}(MCl)+b$, where $2\times10^{-10}$ is the solubility product of silver chloride, $3\cdot4\times10^{-5}$ a constant possibly connected with a complex of the type $AgCl_2$, and *b* is apparently the constant sum of silver chloride in precipitate, in dispersion, and in dissolved molecules. The great difference between this observed total and the minute silver content of filtrates from large precipitates of silver chloride is discussed. It is shown that silver chloride should be most insoluble at 25° in 0·0025*N*-chloride solutions. J. F. S.

**Crystal Structure of Silver Oxide.** RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], **3**, 184—188).—Silver oxide ($Ag_2O$), which crystallises as small, isotropic octahedra, was examined by the *X*-ray powder method, and the type of cubic structure deduced is the same as that assigned to cuprous oxide. The unit cube, containing two molecules of $Ag_2O$, has an edge of 4·768 Å.U.

L. J. S.

**Vapour Pressure of Metallic Calcium.** NORMAN B. PILLING (*Physical Rev.*, 1921, **18**, 362—368; cf. Langmuir, *ibid.*, 1913, **2**, 329; **1914, 4**, 377).—The vapour pressure of calcium was computed

with the aid of Langmuir's expression, which requires measurement of the rate of evaporation of a certain weight of metal of known surface area at constant temperature and in a vacuum. When the coefficient of reflection, *s*, of the calcium molecules from the enveloping walls is taken into consideration, the expression becomes $m=\sqrt{M/2\pi RT}\,.\,p(1-s)$, where $M$ is the molecular weight of the vapour, assumed to be monatomic, $R$ the gas constant, $T$ the absolute temperature, $p$ the pressure in dynes per sq. cm., and $m$ the rate of evaporation in grams per sq. cm. per second. The value of $s$ was determined by control experiments with zinc and cadmium, the vapour pressures of these metals in the solid state being known (Egerton, *Phil. Mag.*, 1917, [vi], **33**, 33). Vapour-pressure curves are given for liquid and solid calcium, the vapour pressure at the melting point, 805°, being 2·0 mm. and the b. p./760 mm. being computed to be 1240°. The calcium employed contained 1·62% of magnesium, 0·009% of iron, and 1·25% of calcium chloride. A. A. E.

**A Simple Process for Obtaining Crystallised Gypsum.** L. Bourgeois (*Bull. Soc. chim.*, 1922, [iv], **31**, 160—161).—Three volumes of nitric acid are diluted with one volume of water and this solution is saturated at just below its boiling point with calcium sulphate. The clear liquid is decanted off and allowed to cool. After eight days, crystals of gypsum begin to appear. W. G.

**Some Compounds in the System $CaO-P_2O_5$ and their Relation to Basic Slag.** Th. Dieckmann and Ed. Houdremont (*Z. anorg. Chem.*, 1921, **120**, 129—149).—A number of compounds of calcium and phosphoric acid have been prepared and examined with respect to their physical properties and solubility in citric acid with the object of throwing some light on the constituents of basic slag. The solubility of tricalcium phosphate, $Ca_3(PO_4)_2$, in 2% citric acid was found to be affected by the temperature to which it was heated. Starting at 94·6%, it fell to 60% as the temperature was raised to 540°, and then rose steadily to 96·2% at the melting point. The composition of the insoluble residue varied in a similar manner, and at the point of minimum solubility had the composition of oxyapatite, $3(Ca_3P_4O_8),CaO$. Further heating to higher temperatures appeared to reconvert this into the normal phosphate. The melting point of tricalcium phosphate is 1670°. Oxyapatite was prepared from a mixture of tricalcium phosphate and calcium carbonate. Formation of the compound was complete at about 1450°, and its low solubility in citric acid, about 55%, confirmed the opinion that this compound is formed during the heating of tricalcium phosphate alone. By melting the oxyapatite with the calculated quantity of insoluble pyrophosphate according to the equation $3(Ca_3P_2O_8),CaO+2CaOP_2O_5=4Ca_3(PO_4)_2$, a highly soluble tricalcium phosphate was obtained. The melting point of oxyapatite is 1540°, *d* 2·99; t crystallises in doubly refracting needles.

Tetracalcium phosphate, $4CaO,P_2O_5$, has a high solubility in

citric acid, but if heated for some time at 1000° the solubility falls to about 25% and the insoluble residue has the composition of oxyapatite. This observation explains earlier statements that tetracalcium phosphate has a low solubility. Its m. p. is 1630°. *It is decomposed by boiling water into lime and oxyapatite.* Calcium pyrophosphate is practically insoluble in citric acid; m. p. 1230°, *d* 3·09. Calcium metaphosphate is also insoluble in citric acid. The molten substance when cooled forms a glass and is difficult to crystallise. The melting point is between 970° and 980°, *d* 2·82 (crystals) and 2·65 (amorphous). Calcium silicophosphate, $5CaO,P_2O_5,SiO_2$, has the same solubility in citric acid as tricalcium phosphate, and is probably therefore a compound of the latter with the normal orthosilicate, $Ca_3(P_2O_4)_2,2CaO,SiO_2$. Its melting point is 1760—1780°. Synthetic fluorapatite, $CaF_2,3Ca_3(PO_4)_2$, has a low solubility, about 10%, in citric acid; m. p. 1630—1650°, *d* 3·18. The above observations show the importance of adding sufficient silica to basic slag to neutralise any excess of lime if a soluble phosphate is to be obtained, since the silicophosphate, unlike tetracalcium phosphate, does not decompose during slow cooling to form insoluble oxyapatite. [See *J. Soc. Chem. Ind.*, 1922, April.] E. H. R.

**Calcium Silicides.** LOTHAR WÖHLER and F. MÜLLER (*Z. anorg. Chem.*, 1921, **120**, 49—70).—It has been shown by a number of workers that, besides the calcium silicide, $CaSi_2$, corresponding with ordinary calcium carbide, a second calcium silicide exists, but various formulæ have been ascribed to it, for example, $Ca_3Si_2$ (Hackspill, A., 1908, ii, 589) and $Ca_{11}Si_{10}$ (Kolb and Formhals, A., 1910, ii, 35). It is now shown that the second compound is calcium monosilicide, CaSi or $Ca_2Si_2$. The compound is formed free from disilicide when a mixture of calcium and silicon in atomic proportions or with excess of silicon up to 100% is heated in a magnesia boat in an atmosphere of carbon dioxide at 1050°. After a quarter of a minute, a violent reaction takes place and the mass becomes incandescent. It must then be cooled rapidly. The mass breaks up readily into small, lustrous, metallic leaflets and larger crystals. The density of the substance, containing a small proportion of uncombined silicon, is 2·346. By dilute acids it is attacked readily with evolution of a spontaneously inflammable silicon hydride and formation of hydrated silica. It is only slowly attacked by concentrated acids, with evolution of hydrogen, and by cold water, more readily by warm water and by dilute ammonia. By contrast, the disilicide dissolves in hydrochloric acid with formation of yellow silicone and without production of spontaneously inflammable silicon hydride. When, in the preparation of the substance, so large an excess of silicon is used as to prevent the necessary rise in temperature during the reaction, a mixture of mono- and di-silicides is formed. From this it was concluded that the monosilicide is formed endothermically from the disilicide. This was confirmed by an experimental determination of their heats of combustion and calculation of their heats of

formation, which were found to be, for $Ca_2Si_2$, +166·3 cal. and fo $CaSi_2$, +208·7 cal.

Pure calcium disilicide can be prepared by heating the mono silicide at 1000—1010° in a current of hydrogen. If excess o silicon is present, this reacts with the calcium hydride formed t give a further quantity of the disilicide. The pure disilicide evolve only hydrogen and no silicon hydride with dilute acid. Th disilicide is stable at least up to 1050°, for at this temperature th monosilicide, in absence of air, dissociates with development of hea into disilicide and calcium.

The silicon hydride formed by the action of dilute acids on th monosilicide is probably silicoethylene formed according to the equation $Ca\vdots Si\vdots Si\vdots Ca + 4HCl = 2CaCl_2 + H_2\vdots Si\vdots Si\vdots H_2$. E. H. R.

**System Ammonia–Magnesium–Mercury. Formation of Magnesium Hexammoniate.** ALBERT G. LOOMIS (*J. Amer. Chem. Soc.*, 1922, **44**, 8—19).—When dilute magnesium amalgam is brought into contact with ammonia, a solid phase separates slowly which has a bright metallic lustre and is decomposed on exposure to air or by reducing the ammonia pressure to below two atmospheres. If the magnesium amalgam contains more than 0·15% of magnesium, the whole becomes completely solid with excess of ammonia, whilst richer magnesium amalgams become solid if more ammonia than 0·035 mol. per 100 grams of amalgam is added. The determination of the composition of the solid phase has been attempted. It is shown that magnesium dissolves in mercury to the extent of 0·323% at 23°. The vapour pressure of the system at 0° has been studied by removing measured volumes of ammonia. The vapour-pressure curve shows a gradually decreasing ammonia pressure as ammonia is removed from which it is concluded that in addition to the vapour phase there are only two phases present, one at least of which is of variable composition. The ratio of ammonia to magnesium has been determined in the crystals and the formula $Mg(NH_3)_6Hg_x$ given to the compound. The solubility of the crystals at 22·4° in pure mercury has been determined and is represented by 0·00593 gram of magnesium per 100 grams of mercury. The ammonia pressure of the crystals has been measured at 22·4°. From the experimental results the value of $x$ in the above formula is calculated as 17·5—18·4. From the large value thus obtained for the amount of mercury, it is concluded that solid solutions are formed by the molecular compound, magnesium hexammoniate, with the excess of mercury present. J. F. S.

**Variously Coloured Modifications of Colloidal Copper.** C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 88—97). —Colloidal copper exists in the following differently coloured modifications: reddish-brown (Lottermoser, A., 1899, ii, 558), blue (Gutbier, A., 1903, ii, 81; 1905, ii, 327), ruby-red (Paal and Leuze, A., 1906, ii, 356), brown (Billitzer, A., 1902, ii, 454), olive (Ehrenhaft, *Anz. Wiener Akad.*, 1902, **39**, 241), and green (Paal and Leuze, *loc. cit.*). The ruby-red variety exists in two forms known as the α- and β-modification, respectively. The

present paper gives a description of the preparation and properties of the α- and β-ruby-red and the blue modifications of copper hydrosol by the use of sodium lysalbate and protalbate and the free acids. The method of converting the ruby-red variety into the blue variety is described. J. F. S.

**German Silver.** WALTER VOIGT (*Z. anorg. Chem.*, 1922, **120**, 309—319).—The equilibrium diagram of the copper–nickel–zinc alloys was investigated by Tafel (A., 1908, ii, 846). All alloys except those rich in zinc were easily worked. The electric resistance was determined after heating the wires to the temperatures of minimum resistance (cf. Credner, A., 1913, ii, 280). If the ratio of copper to nickel remains constant, then increasing amounts of zinc have but little effect. The resistance increases much more rapidly on increasing the nickel content. As regards the thermoelectric effect, if the ratio copper : nickel is constant then increasing amounts of zinc increase it. Increase in the ratio of zinc to copper alone decrease it; a considerable decrease was observed on increasing the nickel content, the copper-zinc ratio being kept constant. In general, the surface of the thermoelectric effect (on diagram) runs parallel to that of the reciprocal of resistance, that is, conductivity. All the alloys showed a solution tension approximately equal to that of copper. They all precipitated copper gradually from a solution of copper sulphate. The passivity of nickels protects the alloy only when its content is 31 mol.% and 43 mol.%. W. T.

**Crystal Structures of the Cuprous Haloids.** RALPH W. G. WYCKOFF and EUGEN POSNJAK (*J. Amer. Chem. Soc.*, 1922, **44**, 30—36).—The crystal structure of cuprous chloride, bromide, and iodide have been deduced from the examination of *X*-ray reflection spectra using films of powder. They are shown to possess the zinc sulphide arrangement and the length of the side of the unit cube is 5·49, 5·82, and 6·10 Å.U. respectively. J. F. S.

**Separation of Isotopes. Theory of Resolution of Isotopic Mixtures by Diffusion and Similar Processes. Experimental *Separation of Mercury by Evaporation in a Vacuum.*** ROBERT S. MULLIKEN and WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1922, **44**, 37—65).—The various phenomena of diffusion and effusion in gases are discussed in connexion with the separation of isotopes. It is shown that for the processes of molecular diffusion through a porous membrane, molecular effusion, and non-equilibrium evaporation, the relative rates of escape of isotopes are proportional to their respective molecular fractions and inversely proportional to the square roots of their molecular weights. In all the above processes, the molecules move independently. As collisions between molecules become more frequent, molecular diffusion passes into capillary transpiration, or mass motion, and non-equilibrium evaporation passes into ordinary distillation. In either case practically no separation of isotopes occurs. If a gaseous mixture of isotopes diffuses into another gas, with no convective mixing, the diffusion coefficients of any two isotopes

are probably in the ratio $x_1/x_2 \sqrt[c]{M_2/M_1}$, where $c$ is a variab quantity usually in the neighbourhood of 1 or 2. The theory complicated, but indicates a higher rate of separation than f molecular diffusion and evaporation, for which $c$ is always 2. further possible method of separation is that of "initial diffusion, which would take advantage of the fact that the front layer molecules diffusing into a gas or a vacuum should be enriche in the lighter isotopes. The theory of non-equilibrium evaporatio is discussed. If the vapour pressures of isotopes when pure a equal, a separation must occur when an isotopic liquid is evaporate in a vacuum in such a way that practically all the evaporatin molecules are condensed. For an efficient separation, good mixin must take place in the surface and body of the liquid. This co sideration makes the method inapplicable to solids, but solutio or liquid alloys might be used. Simple and closely approximat equations are developed for the change in the molecular fractio of any isotope and for the change of atomic weight in a mixtur of any number of isotopes, when the latter is separated into fra tions by a diffusion or evaporation process. A number of equation are evolved which apply to various sets of conditions. The rat of separation of two isotopes as measured by the change of atomi weight for a given operation is proportional to the square of th interval between the molecular weights of the two isotopes, inversel proportional to the ordinary molecular weight and proportiona to the product of the molecular fractions of the isotopes. Simila relations also hold for a mixture of any number of isotopes. Fo a given element, the separation coefficient (equal to the decreas of atomic weight of the isotopic mixture for the first small portio of diffusate or condensate) is inversely proportional to the molecula weight of the compound in which that element is combined. A table of separation coefficients is given, calculated from atomi weights and the results of positive ray analysis. The value give for mercury has been calculated from the present experiment data. Most of the equations developed apply to the separatio by diffusion of any gaseous mixture, whether it consists of isotope or not. In systematic fractionation the diffusate or condensat being formed at any time has an atomic weight less than that c the corresponding residue, which becomes denser as the diffusio proceeds, by a constant amount. Thus the enrichment of th light fraction is a maximum at the beginning. The atomic weigh of the residue increases indefinitely, however, in proportion as th logarithm of its quantity decreases, whilst at the same time th atomic weight of the total diffusate approaches that of the origin material. The use of cuts of two gives equal and opposite enric ments for the two fractions, equal in magnitude to 0·693 time the separation coefficient, or initial enrichment for the light fractior Formulæ are given for calculating the proportions and numbers c isotopic species in compounds containing several isotopic atomi species. Zinc chloride contains twelve molecular isotopes, and i for example, tin has six isotopes, the compound $SnCl_4$ is a mixtur of thirty and $SnCl_2Br_2$ of fifty-four different molecular isotope

existence of many new isomerides due to isotopism is pointed
Experimental work on the partial separation of mercury
isotopes by non-equilibrium evaporation is described. Calcu-
on based on data for a very efficient evaporation gives the
e 0·0057 for the separation coefficient of mercury. The results
ee with those of Brönsted and Hevesy (this vol., ii, 149), but
efficiency of the present separation is better. By making
r successive cuts of approximately two, on both light and
vy fractions, a much larger decrease, of 64 parts per million,
0·013 unit of atomic weight, has been obtained on the lightest
ction and a corresponding increase of 69 parts per million or
14 unit on the extreme heavy fraction. The results are in
nplete agreement with the theory developed. The total differ-
e in density between the extreme fractions is 133 parts per
llion and a difference of 0·027 unit in the atomic weight. Data
given which show that a slight separation of isotopes occurs
ring an ordinary distillation under reduced pressure. A classi-
ation of the possible methods of separating isotopes is given
outline. J. F. S.

**Chromates of Thallium.** G. CANNERI (*Gazzetta*, 1922, **52**, 33—36).—Gröger's method of obtaining basic chromates (A., 20, ii, 313) yields with thallous salts only normal thallous romate. The action of dilute acid on thallous chromate yields allous dichromate, but if a quantity of sulphuric acid insufficient dissolve the chromate is employed and the boiling solution is tered and concentrated, the double salt, $TlHCrO_4,Tl_2CrO_4$, is btained in cinnabar-red crystals, which often form cruciform twins. Thallic chromate may be obtained pure as a golden yellow, rystalline powder by dissolving freshly precipitated thallic oxide excess of chromic anhydride solution.

The *E.M.F.* of the electrode, mercury amalgam|saturated hallous chromate solution varies continuously with the temerature, the curve exhibiting no characteristic point corresponding ith the change in colour which thallous chromate crystals undergo hen heated at 60°. Similarly the conductivity of saturated hallous chromate shows no sudden variation between 25° and 90°. T. H. P.

**Molecular Condition of Metals Dissolved in Mercury.** RANZ SKAUPY (*Z. Elektrochem.*, 1922, **28**, 23—27).—A theoretical iscussion on the views which are at present held with regard to e condition of metals dissolved in mercury. J. F. S.

**Atomic Weight of Yttrium.** H. C. FOGG and C. JAMES (*J. mer. Chem. Soc.*, 1922, **44**, 307—316).—The atomic weight of ttrium has been determined from the ratio $YtCl_3 : 3Ag$, and as mean of twenty-one analyses the value 89·03 is obtained, the xtreme values being 88·97 and 89·08. It is shown that to obtain ery pure yttrium it is essential to use, finally, such a method as e cacodylate separation, in which the yttrium is precipitated hilst the more basic cerium earths remain in the form of quite

soluble salts. The material employed in the present work was obtained from Norwegian gadolinite and was submitted to a long process of purification which consisted in converting the oxalates of the rare earths into sulphates and these into bromates which were subjected to fractional crystallisation. A fraction containing yttrium and erbium bromates and practically no holmium was further purified by fractional precipitation as basic nitrate, which was continued until the erbium bands had practically disappeared. Further fractional precipitations by means of sodium nitrite and potassium ferricyanide were also carried out. The oxide obtained at the end of this series of purifications had a pale cream colour, due to a minute trace of praseodymium oxide, and this was removed by converting into acetate and precipitating as cacodylate, which effectually removed the last trace of impurity. The final purification was attempted by precipitation as the dimethyl phosphate, or *p*-sulphobenzoate and also by crystallisation of the acetate. The two former methods effected no purification, but the crystallisation of the acetates concentrated the coloured oxide in the mother-liquors. It was found, however, to be too wasteful and tedious.

J. F. S.

**[Revision of the Atomic Weight of Lanthanum.] Correction.** G. P. BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 328).—A correction of some eight figures in a table contained in a paper by Baxter, Tani, and Chapin on the atomic weight of lanthanum (A., 1921, ii, 454). The following corrected values are given: $LaCl_3:3Ag=0\cdot757895$; atomic weight of lanthanum=138·914 (mean); $LaCl_3:3AgCl=0\cdot570413$; atomic weight of lanthanum=138·913 (mean).

J. F. S.

**The Separation of the Rare Earths by Basic Precipitation.** WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Z. anorg. Chem.*, 1921, **120**, 120—128).—In a previous paper (A., 1920, ii, 434) a method was given by which lanthanum could be separated from neodymium and praseodymium by regulated precipitation of the basic chlorides by ammonia in presence of ammonium chloride. The investigation has now been extended to samarium and it is found that the solubility of samaria in ammonia–ammonium chloride solutions at different concentrations and temperatures approximates closely to that of the didymia earths, being generally somewhat lower. Attempts to discover an unknown element between neodymium (atomic number 60) and samarium (62) by fractional precipitation of neodymia and samaria were unsuccessful.

With the object of applying the basic precipitation method more widely, the solubilities of lanthana, praseodymia, neodymia, and samaria were examined in presence of ammonia and ammonium nitrate at different temperatures, by adding the calculated quantity of ammonia, according to the equation $M'''(NO_3)_3+3NH_3+3H_2O \rightleftharpoons M'''(OH)_3+3NH_4NO_3$ to the neutral nitrates in 1, 2, 3, 4, and $5N$-ammonium nitrate solutions, and shaking for a day in a thermostat to attain equilibrium. The biggest separation of the solubility curves was found in 4—$5N$-ammonium nitrate solu-

tion at 100°, instead of 2—3*N* at 50° as in the case of the chlorides. The separation therefore depends on the nature of the anion, showing that it is due to the formation of basic salts of varying composition and solubility. The solubilities were then further examined in presence of an equivalent quantity of magnesium or zinc nitrate under similar conditions. The presence of magnesium offered no advantage for the separation of lanthanum from the other earths, but the solubilities of the last differed more among themselves at high concentrations of ammonium nitrate in presence of magnesium nitrate. The presence of zinc nitrate, however, increased the solubilities markedly, especially that of lanthana, which became four times that of the other earths. The practical application of this result will be reported later. E. H. R.

**The Minimum Solubility of Aluminium Hydroxide in Water.** A. Massink (*Chem. Weekblad,* 1922, **19**, 66).—Since the minimum solubility of an amphoteric electrolyte lies at the isoelectric point, which for aluminium hydroxide requires $p_H \pm 7$, waters which are treated with aluminium compounds as coagulants should have a hydrogen-ion concentration close to that value. S. I. L.

**Tempering.** A. Poucholle (*Compt. rend.*, 1922, **174**, 611—613).—Curves are given showing the variation in length of steel wires as a function of the time of cooling after different treatments. Tempering is characterised by the absence of the transformation point $Ar_1$ at low temperature. The transformation of γ-iron into α-iron only takes place at the point $Ar_2$, that is, at about 200°. Over the temperature range 650—200°, from the point $Ar_1$ to the point $Ar_2$, the curves do not show any angular point. However, invariably in this region, and only in this region, mechanical tensions appear, being manifested by sharp cracks and accompanied by the projection of the thin skin of oxide. The transformation point $Ar_1$ is lowered if the annealing observed follows a tempering. Similarly, the temperature at which tempering is obtained is lowered by successive temperings. The amplitude of the inflection $Ar_1$ diminishes (*a*) by rise in temperature until it becomes nil, (*b*) by the duration of the heating if the temperature remains constant. W. G.

**Reduction of Ferric Chloride.** A. Pickles (*Chem. News*, 1922, **124**, 93—94).—When hydrogen is passed through ferric chloride solution containing pieces of fine copper gauze, the ferric chloride is reduced rapidly; varying quantities of cuprous chloride are produced at the same time, and the reaction, which appears to be one of adsorption, is accelerated when the gauze is so arranged that it comes into intimate contact with the hydrogen. W. P. S.

**The System Ferric Oxide–Sulphuric Acid–Water.** Malcolm Percival Applebey and Sidney Herbert Wilkes (T., 1922, **121**, 337—348).

**Examination by the X-Ray Spectrum of Metallic Oxides which are Stable at Red Heat (Prepared by Different Methods and having Different Properties).** J. A. HEDVAL (*Z. anorg. Chem.*, 1922, **120**, 327—340).—That the properties of certain oxides prepared by different methods vary as regards colour, density, etc., is generally explained by assuming the existence of allotropic modifications. As this seems highly improbable, these oxides have been examined by the *X*-ray spectrum. The author shows that identical spectra can only be obtained from the same modification, and vice versa. The following oxides were examined. Ferric oxide (27), ferrosoferric oxide (2), alumina (5), cobaltous oxide (2), cobaltocobaltic oxide (3), nickel oxide (6), magnesia (7), zinc oxide (6), cupric oxide (11), stannic oxide (3). The numbers in brackets give the number of different methods employed in their preparation. No oxide was found to exist in the amorphous form; they were all crystalline or cryptocrystalline. The different preparations of the same oxide gave identical spectra, which were the same as for the minerals. Many oxides were heated at 1150° for some time; this caused a change in some of their properties, but the *X*-ray spectrum remained unchanged. These changes in properties are not caused by changes in structure. W. T.

**Properties of Subsidiary Valency Groups. III. The Preparation, Properties, and Molecular Volume Relationships of the Hydrates and Ammines of Cobalt Fluoride, Bromide, Iodide, Nitrate, Carbonate, and Citrate.** GEORGE L. CLARK and HENRY K. BUCKNER (*J. Amer. Chem. Soc.*, 1922, **44**, 230—244; cf. A., 1921, ii, 116).—The preparation and properties of a number of hydrates and ammines of several salts of cobalt are described. *Cobaltous fluoride trihydrate* is prepared by the action of hydrofluoric acid on cobalt carbonate; it forms rose-red crystals which only lose the last of the water at 300° in a current of nitrogen; $d=2{\cdot}583$. *Cobaltous fluoride hexammine*, prepared by passing dry ammonia over the anhydrous fluoride placed on a balance pan until the requisite weight has been absorbed, which required about twenty-four hours, is a reddish-brown liquid at 25° which solidifies in ice and salt. It is easily soluble in water without hydrolysis, and has $d=1{\cdot}744$. *Cobaltous fluoride triammine* is produced as a light pinkish-brown compound by keeping the hexammine in dry air; at 40° it loses all its ammonia. *Cobalt citrate tetrammine* is prepared by dissolving cobalt citrate in concentrated ammonia and evaporating spontaneously in a vacuum. It is a pink, very stable, crystalline compound, $d=1{\cdot}686$. The preparation of many other compounds which have previously been prepared is also described. The molecular volume of all the above-named componnds is tabulated and the apparent volume of the subsidiary group calculated. The present work furnishes further evidence of the existence of cavities in the space lattice of solids, which may hold secondary valency groups, the sizes of the cavities depending on the relative volumes of kation and anion and varying in a parallel fashion with the stability of secondary

valency compounds. The constant relationship of physical properties among the halogens, free and combined, is shown by the linearity of the molecular volumes of the cobalt haloids, as well as by those of numerous other metal haloids, when plotted against the atomic volume of the halogens at the boiling point. Such linearity is not maintained after the formation of hydrates or ammines. The great importance of the percentage contraction in the formation of hydrates, ammines, and polyhaloids is shown by a straight line proportionality to stability. J. F. S.

**Electrometric Study of the Hydrolysis of some Complex Cobaltammines under the Action of Barium Hydroxide.** PAUL JOB (*Compt. rend.*, 1922, **174**, 613—616).—Electrometric titration of complex cobaltammines with barium hydroxide gives a clear indication when the whole of the water of constitution of the cobalt complex has been replaced by the hydroxyl group. This method is capable of much wider application than the electrical conductivity method previously employed (cf. A., 1920, ii, 320). The curve obtained with the sulphatopentammine nitrate is quite regular and shows no inflexion, whereas the curves obtained with roseopentammine chloride and diroseotetrammine chloride both show marked inflexions and indicate when the replacement of the water of constitution is complete. W. G.

**The Equilibrium of Tungsten and its Oxides with Hydrogen and Water Vapour; Carbon Monoxide and Carbon Dioxide and Oxygen.** J. A. M. v. LIEMPT (*Z. anorg. Chem.*, 1921, **120**, 267—276).—The measurements of Chaudron (A., 1920, ii, 379) are used to calculate the equilibrium constants for the reactions $WO_2+2H_2 \rightleftharpoons W+2H_2O$; $W_2O_5+H_2 \rightleftharpoons 2WO_2+H_2O$; and $2WO_3+H_2 \rightleftharpoons W_2O_5+H_2O$; and the equilibrium curves are constructed. Making use of the water-gas constant $p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$, the constants for the three reactions $WO_2+2CO \rightleftharpoons W+2CO_2$; $W_2O_5+CO \rightleftharpoons 2WO_2+CO_2$; $2WO_3+CO \rightleftharpoons W_2O_5+CO_2$ are also calculated. Further, from the known thermal dissociation of water, the vapour pressures and heats of formation of the three oxides of tungsten are calculated. The vapour pressures at 1773° are: $WO_2 \rightleftharpoons W+O_2$, $p=10^{-8\cdot2}$; $2W_2O_5 \rightleftharpoons 4WO_2+O_2$, $p=10^{-8\cdot0}$; $4WO_3 \rightleftharpoons 2W_2O_5+O_2$, $p=10^{-6\cdot7}$ atm. The heats of reaction are: $W+O_2=WO_2+122{,}800$ cal.; $4WO_2+O_2=2W_2O_5+121{,}400$ cal.; $2W_2O_5+O_2=4WO_3+123{,}000$ cal. E. H. R.

**Relationships between the Different Oxides of Uranium.** PIERRE JOLIBOIS and ROBERT BOSSUET (*Compt. rend.*, 1922, **174**, 386—388).—The decomposition of uranium trioxide, when heated in a vacuum is irreversible and yields the oxide $U_3O_8$ at 502°. The dioxide when heated in oxygen is oxidised very rapidly, the action commencing at about 185°. The only product is the oxide $U_3O_8$. When heated in a current of hydrogen, the oxide $U_3O_8$ shows signs of reduction at 625° and the reduction can be completed at 650°. The only product is the dioxide $UO_2$. In three hours at 1000° in a vacuum the oxide $U_3O_8$ only loses a very small

fraction of its oxygen. To obtain the dioxide by simple dissociatio the oxide $U_3O_8$ must be calcined at 2000° in a vacuum. W. G.

**The Oxides of Uranium.** P. LEBEAU (*Compt. rend.*, 192 **174**, 388—391; cf. preceding abstract).—From a consideration of th work done on the oxides of uranium the author concludes that th only oxides which have a definite existence are $UO_3$, $U_3O_8$, an $UO_2$. The so-called black oxides have the composition $U_3O$ They are stable in air and can be heated at 1000° under atmospher pressure without decomposition. The green oxides prepared a temperatures below 800° contain varying amounts of uraniu trioxide and can undergo change when exposed to moist air, th uranium trioxide present undergoing hydration (cf. Staehlin this vol., ii, 106). W. G.

**The Amphoteric Character of Stannic Hydroxide and it Bearing on the Isomerism of the Stannic Acids.** GEORG ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1922, **121**, 441-449).

**Germanium. III. Germanium Tetrabromide and Ger manium Tetrachloride.** L. M. DENNIS and F. E. HANC (*Chem. News*, 1922, **124**, 66—69, 82—84; *J. Amer. Chem. Soc.*, 192 **44**, 299; cf. this vol., ii, 150).—When bromine vapour is passe over germanium, prepared by reduction of the dioxide wit hydrogen, superficial reaction takes place in the cold, but the mo favourable temperature for the reaction is about 220°. Th germanium tetrabromide which distils over is best purified fro bromine by fractional distillation. It has b. p. 185·9° (corr.) an m. p. 26·1°. It crystallises in small, white, flattened octahed belonging to the cubic system. The liquid substance can be supe cooled considerably, as low as −18°, without crystallising; $n$ 1·6269; $d_{29}^{29}$=3·1315; specific conductivity <0·000078 reciproc ohm. It is very sensitive to water and fumes in air. With dr ammonia gas, it forms a white, solid compound.

Germanium tetrachloride was prepared by passing chlorine ove germanium. Reaction started at 80°, was rapid at 180°, and a 360° the metal became incandescent. The crude product coul not be freed from chlorine by fractional distillation, but the chlorin was removed by passing dry air through the liquid in a suitab apparatus with a condenser to keep back the germanium tetr chloride. The tetrachloride *is a colourless, mobile liquid whic* fumes in air, b. p. 86·5° (corr.), m. p. −49·5°, $n_D^{25}$, 1·3606, $d_{25}^{25}$, 1·87 When the liquid is placed in water, reaction takes place slowl with a peculiar crackling sound. E. H. R.

**Are Tantalum and Columbium Pentachlorides Conductor of Electricity in the Fused State?** WILHELM BILTZ and ARTHU VOIGT (*Z. anorg. Chem.*, 1921, **120**, 71—76).—According to Hamp (A., 1888, 211), tantalum pentachloride is a good conductor, whil columbium pentachloride is an insulator. To test the accurac these observations the two pentachlorides have been prepare uch a manner that moisture was altogether excluded and th

ubstance was distilled out of contact with air directly into the onductivity apparatus. The tantalum pentachloride was preɔared by passing chlorine over a heated mixture of tantalum ɔentoxide and sugar carbon and distilling the pentachloride. It ormed a snow-white mass of crystals which, when melted at ·30—240°, had a conductivity $\kappa=0 \cdot 30 . 10^{-6}$. The platinum ·lectrodes were strongly attacked, but the liquid appeared clear .nd unchanged. Columbium pentachloride was obtained by passng a current of chlorine over columbium sulphide, and, after emoval of the sulphur chloride, distilling the columbium pentahloride. It crystallised in long, yellow needles, and its conluctivity at 220—235° was $\kappa=0 \cdot 22 . 10^{-6}$. The electrodes were .ttacked also in this case. The two compounds are therefore ɔoth insulators of about the same order as the best conductivity vater. E. H. R.

**Action of Selenium on Gold.** H. PÉLABON (*Compt. rend.*, 922, **174**, 391—392).—It is now shown that gold is attacked by elenium if immersed in the latter at a temperature just below its ɔoiling point. The gold fixes some of the selenium, which is only emoved with difficulty on heating, and at the same time some ıf the gold passes into the selenium. The β-selenium previously ecorded (this vol., ii, 141) is, therefore, not a pure compound, ts low electrical resistance being explained by the presence in it ıf gold dust held in suspension and by the crystalline configuration ıf the selenium. W. G.

**Preparation of Chloroplatinic Acid by Means of Hydrogen ᵓeroxide.** PAUL RUDNICK (*J. Amer. Chem. Soc.*, 1921, **43**, ·575—2577).—Details of a method for working up platinum residues .re given. The residues from the determination of potassium .re extracted with the smallest possible quantity of hot water .nd filtered hot to remove asbestos and paper fibre. On cooling, ıure potassium chloroplatinate is obtained as crystals. The iltrate from the crystals and all other aqueous filtrates are reduced ·ith zinc and hydrochloric acid, and after removing the platinum ·lack the filtrates are exposed to sunlight for several weeks, whereby urther quantities of platinum black separate. Alcohol filtrates re treated as above after the alcohol has been expelled. The ranular platinum black is washed and suspended in hydrochloric cid, treated with concentrated hydrogen peroxide, and stirred ·y passing in a stream of hydrogen chloride. The solution of the ıetal is complete in a few hours. The solution is treated with he necessary amount of potassium chloride and the potassium latinichloride added to the quantity obtained above. The ıaterial is stocked in this form. The reagent is prepared by educing a weighed amount of potassium platinichloride with lkaline sodium formate, washing the platinum black, and disɔlving as above. The solution is then made up so that 10 c.c. f the reagent contains 1 gram of metallic platinum. J. F. S.

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## Mineralogical Chemistry.

**The Relation of Chalcedony to other Forms of Silica.** ÈDWARD W. WASHBURN and LOUIS NAVIAS (*Proc. Nat. Acad. Sci.*, 922, **8**, 1—5).—Chalcedony from Yellowstone Park and black ›ebble flint from France were examined in comparison with quartz, ristobalite, tridymite, and silica-glass, and determinations are ive n of *d*, *n*, inversion-temperature, coefficient of cubical xpansion on either side of the inversion-temperature, and change ı volume on inversion. The results suggest that the raw materials onsist of quartz, but that after calcination the material is cristo-alite. This is fully confirmed by the *X*-ray spectra. After alcination at 1450° for two hours, the chalcedony gave 99·87% $iO_2$ and the flint 99·6% $SiO_2$. L. J. S.

**Camsellite, a New Borate Mineral from British Columbia.** I. V. ELLSWORTH and E. POITEVIN (*Trans. R. Soc. Canada*, 1921, ect. IV, [iii], **15**, 1—8).—This is found as white, fibrous masses, ıtermixed with chrysotile and dolomite, filling shear zones in erpentine near Douglas Lake in the Nicola mining division. The lades give straight extinction with negative elongation and are robably orthorhombic; refractive indices α 1·575, γ 1·649. .nalyses I, II, and III are of the camsellite, dolomite, and hrysotile respectively, separated from one another as far as ossible; after deducting considerable amounts of impurities ıese are reduced to I*a*, II*a*, III*a*.

| | $SiO_2$. | $CO_2$. | $B_2O_3$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $H_2O$ (at 110°). | $H_2O$ (>110°). | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 7·65 | 5·64 | 29·07 | 0·26 | 0·86 | 0·95 | 0·85 | 3·69 | 41·72 | 0·52 | 9·88 | 100·12* |
| I. | 1·15 | 46·10 | trace | 0·09 | — | 0·29 | 0·66 | 29·05 | 20·98 | 0·03 | 0·69 | 100·05† |
| I. | 39·95 | 1·15 | trace | 0·32 | 1·44 | 0·13 | 0·06 | 0·75 | 41·43 | 1·80 | 13·04 | 100·08§ |
| I*a*. | — | — | 40·40 | 0·29 | 0·85 | 1·28 | 1·09 | — | 45·24 | 0·26 | 10·55 | 100·00‡ |
| I*a*. | — | 47·25 | — | 0·09 | — | 0·30 | 0·68 | 29·77 | 21·50 | — | 0·41 | 100·00‖ |
| I*a*. | 40·80 | — | — | 0·33 | 1·48 | 0·13 | 0·06 | — | 41·90 | 1·84 | 13·35 | 100·00 |

* Also $Na_2O,K_2O$ 0·03, NiO trace. † Also MgO (insol.) 1·01. § Also $Cr_2O_3$ 0·01, $NiO,B_2O_3,Na_2O$, O traces. ‡ Also $Na_2O,K_2O$ 0·04. ‖ Also $Cr_2O_3$ 0·01.

The formula $2MgO,B_2O_3,H_2O$ given by I*a*, corresponds with at of the manganese borate snssexitc. Up to 550° only 2·95% $_2O$ is lost. The mineral readily fuses to a black, opaque globule; ıd it is soluble in acids. L. J. S.

**Tschermigite (Ammonium-Alum) from Wyoming.** E. IEODORE ERICKSON (*J. Washington Acad. Sci.*, 1922, **12**, 49— ·).—Tschermigite occurs as colourless to white, columnar masses .d imperfect crystals in brown bituminous shale near Wam-tter, Wyoming. It is optically isotropic, *n* 1·457, *d* 1·645. ısociated are a pale yellow ammoniacal jarosite (containing $H_4)_2O$ 1·25%) and crystals of gypsum. Analysis gave (also ıces of $Fe_2O_3,CaO,K_2O,Cl$):

| $l_2O_3$. | $(NH_4)_2O$. | $Na_2O$. | MgO. | $SO_3$. | $H_2O$. | Insol. | Total. |
|---|---|---|---|---|---|---|---|
| 1·57 | 5·23 | 0·21 | 0·13 | 35·11 | 47·82 | 0·06 | 100·13 |

At 105°, the mineral fuses in its water of crystallisation and ses three-fourths of its water; nearly all the water is lost at 0°. The ammonium sulphate commences to decompose at 0°, and on ignition the total loss is 88·06%. Sodium alum when nited gives $Na_2O+Al_2O_3$ presumably as sodium aluminate.

L. J. S.

**Melanovanadite, a New Mineral from Peru.** WALDEMAR INDGREN, L. F. HAMILTON, and CHARLES PALACHE (*Amer. J. Sci.*, 922, [v], **3**, 195—203).—A repetition of the earlier paper (this vol., , 155) giving some additional details. The mineral is hygroscopic; aterial which had been exposed to a moist atmosphere contained *p to 16·6% $H_2O$, of which about 10·5% is lost over sulphuric acid* r at 105°. A new analysis of such material gave:

| $V_2O_4$. | $V_2O_5$. | CaO. | $Fe_2O_3+Al_2O_3$. | $H_2O$ (above 105°). | Total. |
|---|---|---|---|---|---|
| 33·48 | 49·38 | 10·65 | 1·39 | 5·90 | 100·80 |

The melanovanadite has probably been derived from a vanadium sulphide which is present in the black shale; and by its own alteration it gives rise to pascoite ($Ca_2V_6O_{17},11H_2O$). A microscopical examination of polished sections of patronite shows that this is a mixture of three minerals which are probably vanadium sulphides. Measurements of the *monoclinic crystals of melanovanadite give* the axial ratios $a:b:c=0{\cdot}4737:1:0{\cdot}5815$, $\beta=88°\ 37\frac{1}{2}'$.

L. J. S.

**Dewindtite, a New Radioactive Mineral.** ALFRED SCHOEP (*Compt. rend.*, 1922, **174**, 623—625).—This occurs at Kasola, Katanga, Belgian Congo, as a canary-yellow powder intimately mixed with torbernite and a white, powdery material (which resembles impure talc, but contains much alumina—a partial analysis is given). Under the microscope, it is seen to consist of minute scales of rectangular or square outline, *d* 4·8. In the closed tube it yields water and becomes brown, returning to yellow on cooling. Before the blowpipe in the oxidising flame it fuses to a black globule, and in the reducing flame yields beads of lead. It is soluble in nitric acid, and decomposed by hydrochloric or sulphuric acid. The mean of several analyses is given under I;

| | $P_2O_5$. | $UO_3$. | PbO. | $Al_2O_3(Fe_2O_3)$. | CaO. | MgO. | $H_2O$. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 10·01 | 55·50 | 21·74 | 2·06 | 1·32 | 2·75 | 5·82 | 0·40 | 99·60 |
| II. | 10·84 | 60·13 | 23·55 | — | — | — | 5·46 | — | [99·98] |

deducting impurities (represented by the white powdery material), II corresponds with $4PbO,8UO_3,3P_2O_5,12H_2O$. L. J. S.

**Japanese Minerals containing Rare Elements. III. Analyses of Beryl of Naegi, Mino Province.** YÛJI SHIBATA and TAKU UEMURA (*J. Chem. Soc. Japan*, 1922, **43**, 48—62).—Beryl (*d* 2·6 and having no radioactivity) from Naegi in Mino Province gave on analysis:

| $SiO_2$. | $Fe_2O_3$. | $Al_2O_3$. | GlO. | CaO. | MgO. | $Na_2O$. | Ignition. | Total. |
|---|---|---|---|---|---|---|---|---|
| 60·89 | 0·77 | 20·79 | 11·10 | 1·00 | 0·99 | 1·57 | 2·75 | 99·66 |

No alkali metals other than sodium were detected. The author deduce the formula, $5GlO,2Al_2O_3,10SiO_2$, the constitutio $Gl[SiO_3{\cdot}Al(OH){\cdot}SiO_3{\cdot}Gl{\cdot}SiO_3{\cdot}Al{<}^{SiO_3}_{SiO_3}{>}Gl]_2$ being suggested.

K. K.

**Thortveitite, a Silicate of Scandium.** Jakob Schetelig (*Norsk Geol. Tidsskr.*, 1922, **6**, 233—244).—Thortveitite (A., 1912 ii, 56; 1920, ii, 627) is found in felspar quarries in Sætersdalen Norway, as large, greyish-green, prismatic crystals resembling epidote in appearance. These are monoclinic ($a:b:c=0{\cdot}7674:1:0{\cdot}5569$, $\beta=77°\ 28'$) and usually twinned on $m(110)$; *H* 6—7, optically negative, $\alpha$ 1·7561, $\beta$ 1·7926, $\gamma$ 1·8093 (Na). Analysis I by J. Schetelig, II by J. Štěrba-Böhm, and III by F. Tauchert.

| | $SiO_2$. | $Sc_2O_3$. | $Yt_2O_3$. | $(Di,Er)_2O_3$. | $Fe_2O_3$. | FeO. | GlO. | Ign. | Total. | *d*. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 42·9 | 37·6 | 17·7* | | 2·1 | 0·8 | — | 0·4 | 100·9 | 3·57 |
| II. | 45·45 | 42·06 | 8·89† | | 2·83 | — | 0·51 | 0·54 | 100·28 | 3·566 |
| III. | 45·55 | 38·61 | 10·47‡ | 4·26§ | 3·13 | — | — | — | 100·02 | — |

* Mol. wt. 270. † Mol. wt. 320. ‡ Mol. wt. 226. § Mol. wt. 380.

These lead to the diorthosilicate formula $(Sc,Y)_2Si_2O_7$, analogous to that of thalenite (A., 1899, ii, 766). Spectroscopic analysis shows the presence of several other rare-earths, but an absence of cerium, zirconium, etc.

L. J. S.

**The Annaheim Meteorite.** R. A. A. Johnston and H. V. Ellsworth (*Trans. R. Soc. Canada*, 1921, [iii], **15**, sect. IV, 69—92).—This iron, weighing 11·84 kilos., was found in 1916 and probably represents the meteor observed on January 21, 1914. The structure is that of a coarse octahedrite, and the different constituents were studied in detail by the metallographic method. I is the bulk analysis of the iron (also insol. in nitric acid 0·003; Ti,V,Al,Sn absent); II of the kamacite groundmass readily dissolved in 10% hydrochloric acid. The constituents insoluble in this dilute acid were separated into: III, bright, tin-white lamellæ of tænite rich in nickel; IV, tin-white, uncrystallised phosphide (schreibersite) giving ratios near $Fe_5(Ni,Co)_2P_2$; V, long, slender crystals of phosphide (rhabdite?), $(Fe,Ni,CO)_3P$. VI, central portion of a nodule of chromiferous troilite, which in the outer portion is intergrown with 38·71% graphite.

| | Fe. | Ni. | Co. | Cu. | Mn. | Cr. | Si. | P. | S. | C. | Total. | *d*. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 91·51 | 7·84 | 0·46 | 0·08 | trace | 0·001 | 0·002 | 0·219 | 0·012 | 0·01 | 100·12 | 7·873 |
| II. | 93·10 | 6·39 | 0·48 | 0·03 | — | — | — | — | — | — | 100·00 | — |
| III. | 60·74 | 37·38 | 0·67 | 0·64 | nil | nil | nil | 0·65 | — | trace | 100·08 | 7·9 |
| IV. | 61·28 | 25·62 | 0·47 | 0·09 | — | — | — | 13·06 | — | — | 100·52 | 7·2 |
| V. | 40·28 | 41·36 | 0·23 | 0·77 | — | — | — | 15·35 | — | n. d. | 98·68* | — |
| VI. | 62·91 | 0·28 | trace | 0·16 | — | 0·96 | — | — | 35·47 | — | 99·76 | 4·814 |

* Also $SiO_2$ 0·39.

L. J. S.

**The Pitts Meteorite.** S. W. McCallie (*Amer. J. Sci.*, 1922, [v], **3**, 211—215).—This meteorite was observed to fall on April 20, 1921, at Pitts in Wilcox Co., Georgia. Four fragments, weighing

57, 42½, 30, and 2 ounces, were picked up; *d* 7·23. Analyses by E. EVERHART gave I for the metallic portion (forming about 90% of the whole); and II for the stony portion, of which 77·62% consists of pyrrhotite (FeS), the remainder being near to hypersthene in composition.

| | Fe. | Ni. | Co. | Sn. | Cu. | Si. | S. | Mn. |
|---|---|---|---|---|---|---|---|---|
| I. | 0·09 | 0·32 | trace | 0·20 | 0·00 | 0·00 | 28·30 | 0·00 |
| II. | 91·50 | 6·67 | 0·45 | 0·04 | trace | 1·40 | 0·02 | 0·05 |

| | MnO. | $Na_2O$. | $K_2O$. | MgO. | $Al_2O_3$. | FeO [*sic*]. | $P_2O_5$. | $SiO_2$. | C [diff.]. |
|---|---|---|---|---|---|---|---|---|---|
| II | 0·27 | 1·17 | 0·32 | 5·96 | 0·30 | 65·52 | 0·07 | 8·46 | 2·32 |

L. J. S.

## Analytical Chemistry.

**Phenol-red as an Indicator for Acidity of Media.** A. MASSINK (*Pharm. Weekblad,* 1921, **58**, 1133—1136).—The colorimetric determination of $p_H$ in the region 7—8 by means of phenol-red is affected by the electrolyte-content of the solution, the values being too low with low salt-content, and too high with high salt-content. S. I. L.

**Continuous Reading Electro-titration Apparatus.** KENNETH H. GOODE (*J. Amer. Chem. Soc.*, 1922, **44**, 26—29).—An electro-titration apparatus for the determination of hydrogen-ion concentration is described by means of which the *E.M.F.* between a calomel electrode and a hydrogen electrode may be read continuously. The voltmeter consists of a three electrode vacuum valve ("audion"). The three electrode valve consists of a highly exhausted glass bulb containing an incandescent filament surrounded by a grid of fine wire, which is itself surrounded by a metallic plate. A battery of 20—100 volts connected between the plate and filament, through a d'Arsonval galvanometer, produces a current through the plate circuit, the magnitude of which is proportional to the potential of the grid. The filament is connected to a 6-volt circuit containing a resistance which adjusts the current to 1·06 amperes. The current in the plate circuit, $I_p$, may be considered as the sum of a constant current, $I_0$, which is independent of the grid potential and a current $(I_p-I_0)$ which is a linear function of the grid potential. The current $I_0$ is balanced by an equal current in the opposite direction and $(I_p-I_0)$ is measured with the galvanometer which is calibrated to read either volts or Sörensen units directly. The calomel cell is connected to the negative pole of the filament circuit and the hydrogen electrode to the grid. The apparatus as described with a d'Arsonval galvanometer of sensitivity of $10{\cdot}1\times10^{-6}$ amperes for one scale division is sensitive to 0·1 Sörensen unit or 0·006 volt. J. F. S.

**Titrations in Ethyl Alcohol as Solvent.** EDNA R. BISI ESTHER B. KITTREDGE, and JOEL H. HILDEBRAND (*J. A Chem. Soc.*, 1922, **44**, 135—140).—Alcoholic solutions of ac maleic, palmitic, and sulphuric acids, *p*-chlorophenol, and ph have been titrated with an alcoholic solution of sodium etho using the hydrogen electrode as indicator. The hydrogen elect was measured against the electrode $HgHg_2Br_2|N/10KBr$ in alcol Similar titrations of alcoholic solutions of ammonia and anilin alcoholic hydrogen chloride were also carried out. Sharp accurate end-points were obtained, but the titrations take m longer than titrations in aqueous solutions by the same met since the hydrogen electrode requires ten minutes before it rea a constant value. The hydrogen potentials at which a serie indicators changes colour was determined by titrating pairs of above-named substances and using the indicators and then mea ing the potential of the mixture which just gives the colour cha The potential range 0·14—0·45 was measured with aniline hydrogen chloride, 0·45—0·70 and 0·90—0·97 with acetic acid sodium ethoxide and 0·75—0·98 volt with *p*-chlorophenol sodium ethoxide. The positions of most of the indicators in alc are close to their positions in water; some exceptions occur, example, cyanine is displaced very much to the acid side, some indicators which are useful in water cannot be used in alcol solution. The following colour changes and potentials are corded: Benzaldehyde-green, green 0·69 colourless. Bromophe blue, yellow 0·34, green 0·47 blue. Cresol-red, pink 0·20 or 0·30. Curcumin, greenish-yellow 0·66 red 0·85 orange 0·91 gol Cyanine, colourless 0·24 blue; gallein, rose 0·68 violet-l Iodeosin, golden brown 0·20 pink; methyl-green, blue 0·66 laven Methyl-orange, pink 0·20 orange 0·23 yellow. Methyl-vi violet 0·95 colourless. Methyl-red, red 0·54 orange 0·62 yel Naphthol-benzoin, light brown 0·70 blue. *p*-Nitrophenol, col less 0·61 yellow green. Phenolphthalein, colourless 0·68 Resorcin-blue, red 0·39 blue. Rosolic acid, golden 0·58 orange pink. Sodium alizarin-sulphonate, greenish-yellow 0·50 orange rose 0·82 violet. Thymol blue, red 0·30 golden. Thymolphtha colourless 0·82 blue. Trinitrobenzene, colourless 0·68 gol orange. Tropæolin salmon-pink 0·20 orange 0·23 golden, tropæolin OO, pink 0·15 orange 0·20 yellow. Palmitic acid in presence of tripalmitin may be titrated in alcoholic solution sodium ethoxide, using thymolphthalein as indicator. J. F. S.

**Simple Theory of the Nephelometer.** P. V. WELLS (*J. A Chem. Soc.*, 1922, **44**, 267—276).—The theory of the nephelom and its use are considered. It is shown that although the d ratios by reflection and by transmission are equal, both met cannot be used in nephelometry except for an intermediate ra of concentrations. For extremely dilute suspensions, for exam [v]less than $10^{-5}$ gram/c.c., the transmissions are quite insensit 20, hilst the reflection measurement remains sensitive down to t of vision. On the other hand, for very turbid suspens

he transmission probably follows less complicated laws. Although masses in suspension much too small to be detected by the most delicate balance can be easily measured in a Tyndall beam, the precision of such a measurement can never exceed that of the best photometry, that is, about 0·2%. For sensitive and rapid work nephelometry takes its place with other volumetric methods. The phenomena of diffuse reflection and transmission are much more complicated than is represented in the present considerations, but the simple theory presented gives a general idea of the phenomena and may serve as a starting point of a future investigation.

J. F. S.

**Nephelometry. A Nephelometer with Constant Standard.** A. A. WEINBERG (*Biochem. Z.*, 1921, **125**, 292—310).—A new nephelometer and point-source of light are described which embody the best features of the Kober (A., 1917, ii, 266) and Kleinmann (A., 1920, ii, 634) nephelometers, the most striking feature being the introduction of the Lummer-Brodhun prism whereby the two fields are rendered concentric. Nephelometric estimations with such an instrument are comparative and a modified nephelometer is described with a permanent standard. This is attained by replacing one of the tube systems by two Nicols, the lower of which can be rotated relatively to the upper, thus reducing the light to any degree as recorded by a scale on the Nicol prism. For coloured solutions, a slip of coloured glass can be inserted.

H. K.

**Quantitative Analysis by Centrifuge.** OLOF ARRHENIUS (*J. Amer. Chem. Soc.*, 1922, **44**, 132—134).—The estimation of calcium, magnesium, and phosphoric, sulphuric and nitric acids may be effected by precipitating the various substances in the usual way and transferring the precipitate and mother-liquor to tubes 2·5 cm. diameter at the top and provided with a steep funnel below leading to a capillary tube 4 cm. long and 1 mm. diameter. The precipitate is allowed to settle and by means of gentle shaking is, for the most part, caused to settle in the capillary stem. The tube is then centrifuged until the height of the column of precipitate is constant; this usually requires thirty minutes. The height of the column is then read and reduced to the weight standard by comparison with a precipitate similarly obtained from a known weight of the same substance. The method claims no great degree of accuracy, and is suggested as a suitable method of analysis for soil and similar substances.

J. F. S.

**The Penetrability of Filter-paper.** R. C. GRIFFIN and H. C. PARISH (*J. Ind. Eng. Chem.*, 1922, **14**, 199—200).—An apparatus is described for testing the penetrability of filter-paper by observing the time required to pass 100 c.c. of distilled water at 20° through a 2-inch disk of the paper under a constant head of 9 inches of water. The apparatus, which is constructed mostly of lead, consists of an overflow cup connected by a pipe to the under side of a

wire gauze which supports the disk of filter-paper, and is p 9 inches below the top of the overflow cup. The distilled wa fed into the connecting pipe at such a rate that it overflows a cup as well as through the outlet pipe of the apparatus after pa through the filter-paper, and the number of seconds requir collect 100 c.c. at the outlet is timed with a stop watch. It found that the temperature of the water had a marked bearin the speed of filtration, water at 30°, for example, passing thı more than twice as rapidly as water at 0° under otherwise si conditions. The time factor is also important, and even distilled water is used the filtration slows down after a time c to the hydration and expansion of the fibres. A paper v initially had a penetrability of twenty-five seconds had sl down after two hours to one thousand seconds. G. F.

**Estimation of Perchlorate by Rothmund's Method.** ] König (*Z. anorg. Chem.*, 1921, **120**, 48).—In the estimatic perchlorate by reduction with titanous sulphate by Rothm method (A., 1909, ii, 434), it is unnecessary to pass a curre hydrogen or carbon dioxide through the flask if a long, na glass tube is adapted to the reflux condenser to prevent circul of air. For the oxidation of excess of titanous sulphate, ammonium sulphate is better than permanganate in view o fact that the latter may attack the hydrochloric acid, and th the back-titration of silver nitrate in the chlorine determin by the Volhard process a ferric salt must be present. So titanic sulphate is now a commercial product and can be red electrolytically, using lead electrodes, to titanous sulphate.

E. H.

**Comparative Values of Different Specimens of Iodine Use in Chemical Measurements.** C. W. Foulk and Sa Morris (*J. Amer. Chem. Soc.*, 1922, **44**, 221—229).—Iodine pu by several methods, including wet and dry sublimation and dı in the presence of sulphuric acid and phosphoric oxide, has compared by direct titration with sodium thiosulphate with i prepared by Baxter's atomic weight method (A., 1905, ii, 81, Using some new forms of titration flasks and other pieces of appa for handling iodine, it is shown that the maximum diffe between the various specimens and the highly purified iodi 0·024%. It is shown that a rubber stopper may be used in of a glass stopper for closing the flask in which the iodine is titr The usual method, as given in text-books of analytical chemi of drying iodine by exposing it in a desiccator with a drying a is open to criticism if the iodine has previously solidified in presence of water. Powdered iodine when exposed under a jar with water takes up 0·09% of its weight in forty-eight h whilst crystals take up only 0·05% under the same conditio five days. An exposure to sulphuric acid for ten days rem the whole of the water in both cases. It is suggested that s like iodine, which have a measurable vapour pressure at ordi

temperatures, possess peculiar adsorptive properties, due to the fact that a fresh surface is being continually exposed. J. F. S.

**Method of Determining Traces of Oxygen in Hydrogen.** ALFRED T. LARSON and ERNEST C. WHITE (*J. Amer. Chem. Soc.*, 1922, **44**, 20—25).—A rapid and accurate method of estimating traces of oxygen in nitrogen-hydrogen mixtures such as are used in the synthetic manufacture of ammonia is described. The method consists, essentially, in passing the gas mixture through a platinised platinum catalyst which is heated at 305° in a carefully regulated diphenylamine vapour-bath, and measuring the rise in temperature due to the combustion of the hydrogen by means of a thermo-element. The deflexions of a sensitive galvanometer attached to the thermo-element give a measure of the oxygen content of the gas mixture. Concentrations of oxygen as low as 0·001% may easily be determined with an error of 3%. The apparatus was calibrated for a rate of flow of 500 c.c. per minute by adding electrolytic oxygen from an alkali electrolysis to the oxygen-free mixture of nitrogen and hydrogen. By the use of a less sensitive galvanometer, the apparatus may be used for concentrations of oxygen up to about 1%. Precautions necessary for efficient working of the apparatus are indicated. J. F. S.

**The Estimation of Sulphur in Iron Pyrites.** G. CHAUDRON and G. JUGE-BOIRARD (*Compt. rend.*, 1922, **174**, 683—685).—During the dissolution of pyrites in nitric acid or aqua regia, there is always a separation of free sulphur if the temperature exceeds 60°, in the case of marcasite or pyrites containing other metallic sulphides. If, however, the acid is allowed to act at the room temperature, there is no separation of sulphur, but the time required is much longer. W. G.

**A New Method of Estimating Sulphur in Organic Compounds.** H. TER MEULEN (*Rec. trav. chim.*, 1922, **41**, 112—120).—The substance is vaporised or decomposed by heating in a current of hydrogen and the mixture of vapours and hydrogen then passed through a heated quartz tube containing platinised asbestos. All the sulphur is thus converted into hydrogen sulphide, which is led into an alkaline solution and estimated iodometrically. In the case of very small quantities, colorimetric estimation by means of sodium plumbite is suitable. Experimental errors are avoided by using small quantities of material, heating gently, and not allowing the hydrogen to pass too quickly. It is occasionally necessary to burn off a deposit of carbon from the catalyst.

The results obtained by this method are in good agreement with the theoretical values. H. J. E.

**Volumetric Method for the Estimation of Hyposulphurous and Sulphoxylic Acids.** FERRUCCIO DE BACHO (*Giorn. Chim. ind. Appl.*, 1921, **3**, 501—502).—This method is based on the property possessed by formaldehyde of forming with hyposulphite solution highly resistant to oxidation by means of atmospheric oxygen [cf. *J. Soc. Chem. Ind.*, 1922, 250A.] T. H. P.

**Microchemical Estimation of Nitrogen.** C. VALLÉE M. POLONOWSKI (*Compt. rend. Soc. Biol.*, 1921, **84**, 900—901; *Chem. Zentr.*, 1921, iv, 1080).—For microchemical estimatio nitrogen, the substance is heated with 1 c.c. of sulphuric 1 gram of potassium sulphate, and a small piece of quartz, diluted with 6 c.c. of water. After addition of 3 c.c. of so hydroxide solution, the ammonia is carried over by a curre air into 0·02*N*-sulphuric acid. G. W.

**Estimation of Small Quantities of Nitrogen by Kjelda Method.** J. K. PARNAS and RICHARD WAGNER (*Biochem* 1921, **125**, 253—256).—A description of a slight modificatio Pregl's micro-Kjeldahl method of analysis. H.

**Nesslerisation of Ammonia Solutions.** CLARENCE E. and HARRY P. ROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 2574—257 In the estimation of ammonia in urine by the Folin-Bell me (A., 1917, ii, 268) and of urea in urine by the Folin-Young method (A., 1919, ii, 304), the authors were troubled by the f ation of clouds and precipitates during the time (twenty min which the solution is kept after the addition of the reagent. investigation of the reactions shows that such disturbing occurre may be avoided if the following points are observed. Dist water only must be used for dilutions; the flask must be ri with nitric acid before each determination to remove the mer film which may have been formed in a previous experiment; Nessler solution should be the one recommended by Folin Wu (A., 1919, ii, 308); the whole of the Nessler solution mus added rapidly; after the addition, the solution must not be sh or stirred and must be left unmoved for at least twenty mi and any dilution must be made only after this time has ela the solution to be Nesslerised should not contain more than 1·0 of ammonia nitrogen in 150 c.c. On Nesslerisation and dil to 200 c.c., the brown colour is very intense, and with such co trated solutions part of the product tends to deposit on the of the flask and interfere with the colorimetric work. J. F.

**The Volumetric Estimation of Hydroxylamine and H azine.** ALBIN KURTENACKER and JOSEF WAGNER (*Z. a Chem.*, 1921, **120**, 261—266).—It was shown by Rupp and M (A., 1913, ii, 618) that hydroxylamine can be oxidised qu tatively by a bromate-bromide mixture in sulphuric acid sol to nitric acid, according to the equation $NH_2{\cdot}OH+6Br+2H$ $HNO_3+6HBr$. As a method of analysis, however, the rea has serious limitations, since, unless only a very small quantit hydroxylamine is taken and a large excess of bromine used, oxida is incomplete and nitrous acid is formed. It is found, how that if bromate alone is used in strong hydrochloric acid solu nascent chlorine being then the oxidising agent, complete oxida is assured, and the reaction can be used for the estimatio hydroxylamine. The hydroxylamine solution (containing a 1·14 gram of $NH_2{\cdot}OH,HCl$ per litre) is mixed with exces

$0{\cdot}1N$-potassium bromate solution and acidified with hydrochloric acid. After a quarter of an hour (the reaction is not instantaneous), potassium iodide solution is added and the liberated iodine is titrated with thiosulphate. Sulphuric acid cannot be used instead of hydrochloric, and bromide must not be present.

Hydrazine is oxidised by bromate or a bromide–bromate mixture in hydrochloric acid solution instantaneously to nitrogen. The estimation can be carried out exactly as for hydroxylamine, estimating excess of bromate by means of iodide and thiosulphate, or a direct bromate titration can be made using indigo as indicator. The hydrazine solution is mixed with potassium bromide and hydrochloric acid and titrated with $0{\cdot}1N$-bromate solution at about 60°. Towards the end of the titration, a few drops of indigo solution are added and the titration is continued until the colour becomes yellow.

Hydroxylamine and hydrazine may be estimated together. A sample is first titrated as for hydroxylamine, and the bromate equivalent for the sum of the two found. A second sample is then oxidised with bromate in an atmosphere of carbon dioxide and the nitrogen evolved is collected and measured. This gives the amount of hydrazine present and that of the hydroxylamine can be calculated. E. H. R.

**The Action of Nitrous Acid on Iodides in the Presence of Oxygen.** MAURICE LOMBARD (*Bull. Soc. chim.*, 1922, [iv], **31**, 161—169).—When nitrous acid acts on potassium iodide in the presence of oxygen, the nitrous acid is regenerated as fast as it disappears. Without taking slight losses into account, two causes limit the phenomenon. One of these causes is independent of the analyst, and is small but relatively constant. It is the production of a small amount of nitrogen. The other cause, which is of variable importance, depends almost entirely on the method of working. It is the production of nitrate (which may be nil); and it is this which, coupled with the losses by diffusion, leads to such variable results. Thus the estimation of nitrites by the liberation of iodine is impossible in the presence of oxygen. Comparable results might be obtained by working under carefully controlled conditions which would, however, be difficult to realise, and different analysts would probably obtain widely differing results. W. G.

**Estimation of Oxides of Nitrogen [in Air].** V. C. ALLISON, W. L. PARKER, and G. W. JONES (*U.S. Bureau of Mines, Tech. Paper* 249).—The phenoldisulphonic acid method for the estimation of nitrates in water analysis is adapted to the estimation of small quantities of oxides of nitrogen in air. The sample is taken in an evacuated tube of about 250 c.c. capacity, and after the usual analysis has been made for carbon dioxide, carbon monoxide, oxygen, etc., 5 c.c. of 10% sodium hydroxide solution and 5 c.c. of hydrogen peroxide are introduced into the tube, which is then closed with a rubber stopper and rotated to coat the inside with a film of liquid, and is then left for thirty minutes. The contents are then washed through a filter-paper into a 150 c.c. beaker and

evaporated just to dryness. The residue is treated with 2 c.c. ‹ the phenoldisulphonic acid reagent, diluted to 10 c.c., filter‹ into a Nessler tube, 15 c.c. of ammonia are added, and the who made up to 100 c.c. and compared with standards similarly prepar‹ from a standard potassium nitrate solution. The method is sens tive to 10 parts of oxides of nitrogen in 1,000,000 parts of air wi‹ an accuracy of about 5 parts per million. G. F. M.

**The Argentometric Titration of Phosphoric Acid.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 205—215).—The soh bility product of silver phosphate in water is of the order $1 \times 10^{-2}$ accurate determinations are impossible, since decomposition occur the salt becoming black. Accurate results are easily obtained i estimating phosphoric acid by means of excess of silver nitrate the solution is made neutral to phenol-red by addition of 0·1N sodium hydroxide; phenolphthalein is less suitable. In place ‹ sodium hydroxide, sodium acetate may be added; about 2 gran are required for 10 c.c. of 0·1 molar phosphate solution, and in th case ammonium, calcium, and magnesium salts do not interfere.

In estimating phosphoric acid in urine, the ammonium ma‹ nesium salt is precipitated, washed and dissolved in nitric aci‹ the solution being neutralised with sodium hydroxide, usir dimethyl-yellow as indicator, and titrated with silver nitrate, tl excess of which is estimated by Volhard's method. S. I. L.

**Errors caused by Nitrates and Nitrites in the Estim‹ tion of Arsenic by the Distillation Method and a Means f‹ their Prevention.** J. J. T. GRAHAM and C. M. SMITH (*J. Ind. En Chem.*, 1922, **14**, 207—209).—In the presence of nitrates or nitrit‹ the distillation method for the estimation of arsenic as usual carried out, using cuprous chloride or cuprous chloride and ferro‹ sulphate as the reducing agents, gives low results owing to son volatile substance, probably nitrosyl chloride, carried over wi‹ the arsenic trichloride into the distillate oxidising it to quinqu‹ valent arsenic. The extent of the oxidation depends largely c the length of time the distillate is kept before titration. Tl error may be avoided by using hydrazine sulphate in conjunctic preferably with sodium bromide as the reducing agent, whereb the nitrates, etc., are reduced to nitrogen. For a sample co‹ taining the equivalent of not more than 0·6 gram of $As_2O_5$, 50 c.‹ of a solution containing 2% each of hydrazine sulphate and sodiu‹ bromide in dilute (1 : 4) hydrochloric acid will be required for tl analysis. The mixture is boiled for two to three minutes, 100 c.‹ of concentrated hydrochloric acid are added, and the distillatic is proceeded with in the usual way. G. F. M.

**The Separation of Arsenic from Tungsten, Vanadium, an Molybdenum by Means of Methyl Alcohol in a Current of Ai** L. MOSER and J. EHRLICH (*Ber.*, 1922, **55**, [*B*], 430—437).—I has been shown previously (A., 1912, ii, 866) that tervalent arseni ‹n be separated quantitatively from antimony and other meta ‹he temperature of boiling water by volatilising it partly ‹

methyl arsenite and partly as arsenic trichloride in a current of air. In the presence of tungstic acid, however, the removal of arsenic is incomplete, owing to the adsorption of a portion of the arsenic trichloride by colloidal tungstic acid. The difficulty can be removed by bringing the latter into highly disperse solution, which is readily effected by means of pyrogallol; the procedure is described fully in the original. Accurate results are obtained thereby in the estimation of arsenic, but the method suffers under the disadvantage that the pyrogallol must be destroyed before the tungsten can be estimated in the residue. The action of a number of other substances (oxalic, tartaric, and citric acids) is considered and the following process is recommended. The solution containing the tungstate and arsenious acid (arsenic acid must be reduced by one of the customary methods) is evaporated to small bulk and treated with glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (120—150 c.c.); after addition of methyl alcohol (30 c.c.), distillation is effected as described previously in a current of air. Arsenic is estimated, preferably iodometrically, in the distillate; the residue in the distillation flask is evaporated completely to dryness on the water-bath, dissolved in dilute sodium hydroxide solution, and the tungstic acid precipitated as mercurous tungstate.

The separation of arsenic from molybdenum and vanadium is effected without difficulty by the ester method; it is only necessary to make certain that a sufficient amount of the reducing agent is added (even when the arsenic is present in the tervalent state), since molybdic and vanadic acids themselves attack the latter.

H. W.

**The Theory of the Distillation of Arsenic and a New Separation of Arsenic from all Metals in a Current of Air.** L. MOSER and J. EHRLICH (*Ber.*, 1922, **55**, [*B*], 437—447; cf. Moser and Perjatel, A., 1912, ii, 866; Moser and Ehrlich, preceding abstract).—A study of the rate of distillation of arsenic chloride from a solution of arsenious oxide in concentrated hydrochloric acid shows that the process is influenced greatly by the hydrolysis of the chloride and that this effect becomes more marked as the distillation proceeds towards completion. The difficulty has been overcome largely by suitable addition of potassium bromide to which a catalytic action has been commonly ascribed. Its function, however, is shown to depend on its ability to repress hydrolysis of arsenic chloride, since it may be regarded as attracting the water from the mixture for purposes of solution and thus rendering the solutions of arsenic chloride in hydrochloric acid more concentrated with regard to the latter. The effect is exhibited by a number of other substances, for example, barium chloride, barium acetate, sodium pyroborate, sodium benzoate, sodium nitroprusside, crystalline lactose, etc., which are freely soluble in water, but insoluble or very sparingly soluble in concentrated hydrochloric acid.

The following method of estimating arsenic is recommended.

It does not involve the use of methyl alcohol. It requires no supervision and is complete within about forty minutes (or thirty minutes after addition of potassium bromide). Since the liquid never comes to its boiling point, it is impossible for compounds of antimony to distil. The apparatus consists of a wide-mouthed flask of 300 c.c. capacity provided with a rubber stopper carrying an inlet tube for air, a stoppered dropping funnel, and a bulb tube connected with a long glass tube dipping into water (250 c.c.) contained in a beaker which is cooled by running water. The arsenious oxide (0·15—0·25 gram) is dissolved in concentrated hydrochloric acid (*d* 1·19, 50 c.c.) in the flask which is immediately immersed up to the neck in boiling water, whilst a brisk current of air is passed through the solution. At intervals of ten minutes, further additions of concentrated hydrochloric acid (20 c.c.) are made. After forty to sixty minutes the distillation is interrupted and the arsenic titrated in the distillate with *N*/10-potassium bromate solution. The procedure is similar when potassium bromide (about 1·5 grams) is used, but two or at most three additions of hydrochloric acid only are necessary. Arsenic acid must be reduced in the usual manner, for example, with ferrous sulphate, hydrazine sulphate, or even with potassium bromide alone. H. W.

**Microchemical Estimation of Carbon and Hydrogen.** FRITZ WREDE (*Ber.*, 1922, **55**, [*B*], 557—563).—A valuable detailed discussion, unsuitable for abstraction, of apparatus, absorbent and oxidising materials, and procedure necessary for the microchemical estimation of carbon and hydrogen in organic compounds by Pregl's method. J. K.

**Estimation of the Carbon Dioxide Content of Air, with Special Reference to the "Aeronom."** HANS RAUCH (*Z. Hyg. Infektionskrankh*, 1920, **91**, 1—26).—A critical comparison was made between various methods for the estimation of carbon dioxide as used in analysing the air of schools, dwellings, etc. Results obtained with the "aeronom," an instrument in which the difference of pressure, measured with an oil manometer, of an enclosed volume of air before and after its content of carbon dioxide has been absorbed with sodium hydroxide, differ by as much as 20% when compared with the more exact Pettenkofer's baryta method. These larger errors were found also when the carbon dioxide was absorbed by sodium carbonate or sodium hydroxide as in the methods of Lung-Zeckerdorf and Wolput. The author concludes that of the methods studied in determining the ventilating conditions in rooms, Pettenkofer's method is preferable.

CHEMICAL ABSTRACTS.

**Estimation of Carbon Dioxide in Mineral Carbonates.** L. A. SAYCE and A. CRAWFORD (*J. Soc. Chem. Ind.*, 1922, **41**, 57—58T).—The ignition method in a Teclu furnace until the substance shows no further loss in weight gives consistent results where the decomposition temperature is low enough for it to be

applied without complications arising, as, for example, reduction to metallic lead with cerussite, and oxidation of the ferrous oxide to an unknown extent with chalybite. The Schrötter method is unsuitable for estimating the carbonates of metals having comparatively insoluble sulphates. Hydrochloric acid can be used successfully for the decomposition, but this introduces the danger of loss of acid by volatilisation. Armstrong's simple modification of the Schrötter apparatus is capable of fair accuracy. Garrett's apparatus, consisting of a stout test-tube to the top of which is attached a Y-tube, one branch of which bears a tap funnel containing dilute acid, and the other a combined condenser and drying tube leading to potash bulbs or soda-lime tubes, gave good results with witherite, but for some unexplained reason very inconsistent results were obtained with calcite. Collin's calcimeter, by reason of the ease of operation, and the short time needed for an estimation seems well adapted for dealing with readily soluble carbonates when an accuracy of 0·1 or 0·2% is sufficient. G. F. M.

**The Volumetric and Gravimetric Estimation of Zinc.** STEFAN URBASCH (*Chem. Ztg.*, 1922, **46**, 6—7, 29—30, 53—55, 97—99, 101—103, 125—127, 133—134, 138—139).—The separation of zinc from the common metals and its estimation by means of potassium ferrocyanide and sodium sulphide and as zinc oxide have been studied in detail. In all cases the ore is dissolved in aqua regia, the solution evaporated with sulphuric acid, the heavy metals removed with hydrogen sulphide and the iron and aluminium with ammonia in the presence of ammonium chloride if the ferrocyanide or gravimetric method is to be used, or of magnesium chloride if the sulphide titration is adopted. The ferrocyanide titration is carried out in a bulk of 150 c.c. containing 2—3 drops of hydrochloric acid and 3 c.c. of a 0·03% ferric chloride solution. The ferrocyanide is added to the boiling zinc solution until the blue colour just fades to white, a standard zinc chloride solution is then added, drop by drop, until the blue colour just reappears, and this amount of zinc is deducted from that found in the first titration. In the sulphide method, ammonia and ammonium salts should be kept as low as possible. The separation of cadmium from zinc by hydrogen sulphide is not complete in one operation if much zinc is present, but a satisfactory separation may be obtained by boiling the solution of the mixed metals with aluminium foil and finally adding hydrogen sulphide water to prevent resolution of the cadmium. The separation of zinc from nickel and cobalt by the "salting out" method is discussed with regard to the necessary acidity of the solution; the author recommends saturating a solution containing less than 0·15 gram of zinc and about 1 c.c. of normal acid per 100 c.c. with hydrogen sulphide at 50°. [Cf. *J. Soc. Chem. Ind.*, 1922, 218A.] A. R. P.

**The Detection of Small Quantities of Lead in Urine.** O. SCHUMM (*Z. physiol. Chem.*, 1922, **118**, 189—214).—Copper sulphate is added to the urine and the lead precipitated with the copper as the sulphides by hydrogen sulphide; by then separating the

mixture by electrolysis, it is possible to detect small quantities lead of the order of a few decimilligrams in a litre and a half.

S. S. Z

**Studies on Thallium Compounds. I. Analytical.** ARTH JOHN BERRY (T., 1922, **121**, 394—399).

**A New Iodometric Method for the Estimation of Copp** RUDOLF LANG (*Z. anorg. Chem.*, 1921, **120**, 181—202).—The us iodometric method for estimating copper depends on the reduct of a cupric salt by an iodide to cuprous iodide followed by titrat of the free iodine formed. The reaction $Cu^{\cdot\cdot}+2I' \rightleftharpoons CuI+I$ however, reversible, and in the present paper methods are develo for estimating copper which consist in oxidising a cuprous s with a known quantity of iodine and titrating the excess. T most suitable salt for oxidation is cuprous thiocyanate, the react being carried out in presence of ammonium oxalate or tartra The reaction is complicated, however, by the possibility of reaction between thiocyanate and iodine such as $KCNS+8I$ $4H_2O=H_2SO_4+ICN+KI+6HI$. A lengtby investigation v carried out to study the extent to which this reaction proceeds presence of thiocyanates of potassium, sodium, and ammoniu oxalic acid, ammonium oxalate, ammonium sulphate, nitrate, a chloride in presence and absence of copper salts, and it was fou that the reaction could be altogether inhibited in presence of oxa acid and the ammonium salts of strong acids, including ammoni thiocyanate in high concentration. The following method was fina adopted for the estimation of copper. A solution of cupric sa weakly acidified with a mineral-acid, and containing at most 0 gram of copper is reduced with excess of sulphurous acid and dilut to $0{\cdot}1N$. Ammonium thiocyanate solution is added to precipit the copper as cuprous thiocyanate and the solution is boiled expel sulphur dioxide. After cooling, a mixture of 5 volumes ammonium oxalate solution containing 45 grams of hydrated s per litre and 7 volumes of oxalic acid solution containing 120 gra of hydrated acid per litre is added, and the whole is diluted 400 c.c. Next $0{\cdot}1N$-iodine solution is run in until a clear soluti is obtained, the mixture being well shaken, and excess of iod is titrated with thiosulphate solution.

The cupric salt can be reduced with cyanide instead of sulphur acid, the advantage of this method being that the reduction selective for copper and that the reducing agent need not removed. Conditions were determined experimentally under wh reaction between cyanide and iodine is prevented, and it w found necessary, after reduction, to acidify before adding iodi since only cyanogen ions, not hydrocyanic acid, reduce iodi The following method was finally adopted. The cupric salt soluti containing at most 0·28 gram of copper is made ammoniacal in long-necked flask and reduced with $0{\cdot}5N$-potassium cyanide so tion. After addition of 1 gram of ammonium thiocyanate, t solution is acidified with concentrated oxalic acid solution, keepi

old, so that all the copper is precipitated as thiocyanate. The oxidation with iodine and titration are then carried out as above.

In place of the expensive potassium iodide solution of iodine, a potassium cyanide solution can be used, prepared by dissolving 3 grams of potassium cyanide in a little water, dissolving in this 12·7 grams of iodine, and making up to a litre. This solution is quite stable.

The above methods are applicable in presence of all the commoner metals. Notes are given of slight precautions and modifications necessary in presence of silver, mercury, lead, bismuth, arsenic, antimony, cobalt, manganese, iron, barium, strontium, calcium, and magnesium. E. H. R.

**A Rapid Iodometric Estimation of Copper and Iron in Mixtures of their Salts.** IAN WILLIAM WARK (T., 1922, **121**, 358—363).

**Estimation of Metallic Aluminium and Aluminium Oxide in Commercial Metal.** H. V. CHURCHILL (*J. Ind. Eng. Chem.*, 1922, **14**, 81); JULIAN H. CAPPS (*ibid.*, 81—82).—The first author criticises a recent paper by Capps (A., 1921, ii, 657), whose results indicate an atomic weight of 26·81 for aluminium, and concludes that the method described is untrustworthy. Capps replies, admitting an error pointed out by Churchill, but considers that his figures after recalculation still support his contention that the accepted atomic weight for aluminium is wrong. W. P. S.

**The Analysis of Aluminium Alloys.** ANTON BRENNER (*Chem. Ztg.*, 1922, **46**, 188).—*The solution of aluminium and zinc hydroxides in alkali hydroxide solution is treated with sodium* sulphide, the precipitate is collected on a filter, washed with hot water, and dissolved in dilute hydrochloric acid. The cold solution is treated with sodium carbonate and the precipitated zinc carbonate collected, washed, ignited, and weighed as zinc oxide. The method is more rapid than that involving separation of the zinc sulphide from organic acid solutions. A. R. P.

**The Separation of the Oxides of Iron and Aluminium from Admixture with Calcium Oxide by the Nitrate Method.** CHARRIOU (*Compt. rend.*, 1922, **174**, 751—754).—In St. Claire Deville's method for the separation of the oxides of iron and aluminium from calcium oxide by means of ammonium nitrate, it is preferable to carry out the drying, after the precipitation of the hydroxides with ammonia, at a temperature not exceeding 50° and in the presence of ammonium nitrate. The residue is then extracted three times with a boiling 10% solution of ammonium nitrate and subsequently washed with boiling water. Under these conditions the separation is complete. W. G.

**A New Quantitative Method for the Estimation of Iron in the Blood.** ANSON L. BROWN (*J. Amer. Chem. Soc.*, 1922, **44**, 423—425).—To 0·5 c.c. of blood, laked in 4 c.c. of water, 1 c.c. of concentrated hydrochloric acid and 0·01 gram of potassium chlorate

are added, and the mixture is heated in a boiling water-bath u it becomes white or light yellow and the whole of the prote are precipitated. The mixture is allowed to cool and is filter and the residue is washed with water until 15 c.c. of filtrate obtained. The iron is estimated colorimetrically in an aliq portion of the filtrate against a standard iron solution, using pota ium thiocyanate as indicator. W. G

**Separation of Germanium and Arsenic.** JOHN H. MÜLL (*J. Amer. Chem. Soc.*, 1921, **43**, 2549—2552).—A method separating minute traces of arsenic from germanium is describ The method consists in adding a large excess of hydrofluoric ac to the mixed oxides and precipitating cold with hydrogen sulphic By these means arsenic is precipitated quantitatively. Hydrog sulphide is without action on solutions of fluorogermanic a and its salts. The separation is sufficiently accurate to estima as little as 0·01% of arsenic in germanium compounds. T method is especially useful in connexion with the preparation pure germanium compounds, as the fractional crystallisation the double fluoride can thus be avoided and the operation carri out in small volumes of solution. Germanium dioxide is nc toxic, and solutions of it when injected subcutaneously show marked erythropoietic action. J. F. S.

**Co-precipitation of Vanadic Acid with Ammonium Pho phomolybdate.** J. R. CAIN and J. C. HOSTETTER (*J. Am Chem. Soc.*, 1921, **43**, 2552—2562).—The authors have investigat the conditions under which the simultaneous precipitation vanadic acid and ammonium phosphomolybdate is best carri out in connexion with the method of estimation of vanadium steel (A., 1912, ii, 1101). The ratio of vanadium to phosphor in the precipitate has been determined for mixtures in which t phosphorus is constant and the vanadium varies, and for mixtur in which the vanadium is constant and the phosphorus vari The influence of dilution, temperature, and acidity of the solutio has also been investigated. The results show that the co-precipi ation of vanadic acid with ammonium phosphomolybdate may explained as a phenomenon resulting from a partition of t vanadic acid in some undissociated form between the solution an the solid phase. The maximum absorption by the solid pha occurs at a temperature of 40—50° and in a nitric acid conce tration of $4N$. The effect of dilution in lowering the amount occlusion is a direct result of the partition law and can be minimise by the presence of ammonium nitrate, the latter probably tendin to repress the dissociation of the vanadium complex which i occluded. The ammonium vanadophosphomolybdates are prob ably a series of solid solutions the end members of which may b ammonium phosphomolybdate and ammonium phosphovanadate. J. F. S.

**Estimation of Methyl Alcohol.** KARL H. A. MELANDE (*Svensk. Pappers Tid.*, 1921, **24**, 277—278).—A mixture of 22 gram

iodine and 5 c.c. of the solution containing about 2% of methyl :ohol is heated for half an hour at 70° in a slow current of hydrogen, e flask having previously been connected with a condenser, wash-bottle containing a little red phosphorus in water at 50°, d an absorption apparatus containing a few c.c. of pyridine. or a further period of half an hour a higher temperature is nployed, and the current of hydrogen increased. The pyridine lution is concentrated on a water-bath, dissolved in water, and trated with 0·1*N*-silver nitrate solution.

CHEMICAL ABSTRACTS.

**Vapour Pressures of Dilute Alcohol Solutions.** R. THOMAS *J. Soc. Chem. Ind.*, 1922, **41**, 33—34T).—A rapid method of etermining the partial pressures of alcohol and water in aqueous olutions of alcohol is described. This method also constitutes method of analysing air containing water and alcohol vapour. t depends on the facts that water is retained by a layer of calcium arbide which has no action on alcohol, and that alcohol is completely absorbed by a layer of ignited alumina or by passing it hrough 98% sulphuric acid. The process is carried out by passing lry air, free from carbon dioxide, through a bubbler containing the alcohol solution at a rate of 4—5 litres an hour and thence over calcium carbide contained in a U-tube and finally through 98% sulphuric acid or over ignited alumina in a U-tube. The loss of weight of the alcohol bubbler gives the total weight of vapour, and the increase in weight of the sulphuric acid or alumina gives the weight of alcohol. It is essential that fresh carbide be used in each experiment, for calcium hydroxide would retain some of the alcohol. It is shown for solutions containing 5% and 10% of alcohol that the partial pressure of the alcohol is approximately proportional to its concentration. From the data obtained, a table has been constructed showing the ratio of the concentration of alcohol in the gaseous phase to its concentration in the liquid phase for the temperature range 15—26°. J. F. S.

**Estimation of Glycerol in the Presence of Sugars.** L. F. HOYT and H. V. PEMBERTON (*J. Ind. Eng. Chem.*, 1922, **14**, 54—56).—A method is described for the estimation of glycerol in transparent soaps, which almost invariably contain added sucrose. The soap is dissolved in water, the solution acidified with sulphuric acid, and boiled to remove any alcohol which may be present. The mixture is filtered to separate insoluble fatty acids, the filtrate treated with a small quantity of silver sulphate, diluted to a definite volume, and again filtered. A portion of this filtrate is oxidised in the usual way with potassium dichromate–sulphuric acid mixture, using a larger excess of the oxidising mixture than is customary in glycerol analysis; this estimation gives the sum of the glycerol and sugar, and the latter is then estimated separately in another portion of the filtrate. W. P. S.

**Sensitive Test for Phenols.** JAMES MOIR (*J. S. African Chem Inst.*, 1922, **5**, 8—9).—Five c.c. of *p*-nitroaniline hydrochloride

solution (1·5 grams of *p*-nitroaniline dissolved in a mixture 40 c.c. of hydrochloric acid and 500 c.c. of water) are treated w dilute sodium nitrite solution until decolorised, and the mixt is then added to the solution to be tested; an orange-colou precipitate is formed if much phenol is present. After one min an excess of sodium hydroxide is added: a coloration devel varying in depth from salmon-pink to ruby-red, according to quantity of phenol present. The salmon-pink coloured solut exhibits a broad absorption band at λ 494 and this serves to tinguish phenol from the cresols, etc. The test will detect 1 p of phenol in 1,000,000 parts of solution. W. P. S

**Proteinogenous Amines. XIV. A Microchemical Colo metric Method for Estimating Tyrosine, Tyramine, a other Phenols.** MILTON T. HANKE and KARL K. KOESSL (*J. Biol. Chem.*, 1922, **50**, 235—270).—The colour reaction gi by phenol, *o*-, *m*-, and *p*-cresols, and *p*-hydroxyphenylacetic, *p*-hy oxyphenylpropionic and *p*-hydroxyphenyl-lactic acids with sodi *p*-diazobenzene sulphonate may be used for the colorimetric esti ation of these substances. The details of the method are pract ally identical with those previously described for the estimat of iminazole derivatives (A., 1920, ii, 67). Tyrosine and tyram give with a solution of diazobenzenesulphonic acid in sodi carbonate a pink coloration which rapidly changes to yell Addition of sodium hydroxide produces an intensification of yellow and a restoration, to a small extent, of the pink colorati but at no stage is the intensity proportional to the concentrat of the phenol. If, however, sodium hydroxide and then hydrox amine hydrochloride are added to the solution, an intense blui red colour is obtained which is proportional to the amount tyrosine or tyramine present. The coloration so produced m consequently be employed for the estimation of small quantit of these two compounds. Ammonium salts, leucine, glyci hydrogen peroxide, formaldehyde, acetaldehyde, acetone, ace acetic acid, dextrose, and alcohols interfere with the colour. explanation based on a tautomeric change of the keto-enol ty is tentatively advanced to account for the colour changes descri in the case of tyrosine and tyramine. E. S.

**Proteinogenous Amines. XV. A Quantitative Meth for the Separation and Estimation of Phenols includi Phenol, *o*-, *m*-, and *p*-Cresols, and *p*-Hydroxyphenylacetic, Hydroxyphenylpropionic and *p*-Hydroxyphenyl-lactic Acid Tyrosine, and Tyramine.** MILTON T. HANKE and KARL KOESSLER (*J. Biol. Chem.*, 1922, **50**, 271—288).—The meth of separation described was designed to render possible the appl ation of the author's method for the estimation of certain pheno substances (preceding abstract) to mixtures of these substanc a is intended primarily for use in bacterial metabolism studi tyrosine and is not applicable to more complex liquids such Est or blood. The liquid containing the mixture of phenols (Svensk and distilled, whereby phenol and the cresols pass ove

[N]on-aminophenolic acids are removed from the residual liquid [b]y extraction with ether, after which it is made alkaline with sodium [c]arbonate and extracted with amyl alcohol. Tyramine is thus [r]emoved, whilst tyrosine remains in the alkaline solution. Separ[a]tion is thus effected into four fractions. If, as will normally [b]e the case in bacterial metabolism experiments, only one member [o]f each fraction is present, the estimation is proceeded with after [a]ppropriate treatment of the various solutions. The method [f]ails, however, in those cases where more than one member of [e]ach fraction is present since further separation is impossible.

E. S.

**Estimation of Sugar in Small Quantities of Blood by the Pavy-Sahli Method.** SVEND HUBERT REIST (*Schweiz. med. Woch.*, **51**, 419—423; from *Chem. Zentr.*, 1921, iv, 1056).—0·1 c.c. of blood is washed into a test-tube with 3 c.c. of alcohol. The mixture is shaken for half an hour, filtered through hardened filter-paper, and the residue washed twice with 2 c.c. of alcohol. The alcohol is then removed over a water-bath and 0·3 c.c. of Pavy's solutions and 1·8 c.c. of water are added. The liquid is heated to boiling and while boiling titrated with standard (approximately 0·1%) dextrose solution. G. W. R.

**Estimation of Lævulose (Fructose) in Straw.** S. H. COLLINS (*J. Soc. Chem. Ind.*, 1922, **41**, 56—57T).—The colouring matters present in this case bear a high ratio to the sugar and attempts to obtain concentrated solutions sufficiently translucent for the polarimeter failed. It was found in practice that a solution obtained by continuous extraction, of which 10 parts of liquid represented 1 part of straw, was as dark as could be used even with a 200 mm. tube and a quartz wedge saccharimeter illuminated by a 100 c.p. electric lamp. By means of hot and cold water circulating through the jacketed polarimeter tube, temperatures of about 70° and 10°, constant to a fraction of a degree, could be obtained, and ten readings were taken in order to reduce chance errors to unimportance. A serious error was found to be due to the deflexion of the zero by temperature alterations. This was traced to the end glasses of the polarimeter tube and was overcome by annealing them for three hours at 300°. The least trace of alkalinity must be avoided, otherwise the lævulose solutions become almost black at the higher temperature. Faint acidity is not of so much consequence. With straw containing 5—7% of lævulose the error in the estimation is about 0·05% with carefully annealed end glasses. The results of the investigation have shown that with straws containing much sugar three-fourths of the total is lævulose, but when the total sugar is low in amount, lævulose is absent. G. F. M.

**Micro-estimation of Lactose by means of Potassium Permanganate. Application to Milk.** G. FONTÈS and L. THIVOLLE (*Bull. Soc. Chim. Biol.*, 1922, **4**, 23—42).—The author's method for the estimation of dextrose in blood (A., 1921, ii, 563

can, with slight modifications, be used for the estimation of lactose in milk. E. S.

**A Simpler Method of Determining Acetyl Values.** LEON W. COOK (*J. Amer. Chem. Soc.*, 1922, **44**, 392—394).—A modification is given of André's formula (cf. A., 1921, ii, 419) for calculating the acetyl value of an oil from its saponification values before and after acetylation. The new formula is $A=(S'-S)/(1-0\cdot00075S)$, where $A$ is the acetyl value, $S$ the saponification value before acetylation, and $S'$ the value after acetylation. Similarly, the percentage of alcohol in the original sample may be calculated by the formula: percentage of alcohol $=M(S'-S)/(560-0\cdot42S')$ provided that the molecular weight, $M$, of the alcohol is known. W. G.

**The Estimation of Fatty Acids Based on their Volatility in Steam.** W. ARNOLD (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 345—372).—From a large number of determinations of the Reichert-Meissl and Polenske values of pure fatty acids, using the Polenske apparatus and weights of fatty acid varying from 0·01 gram to 0·05 gram, it appears that butyric and hexoic acids only give a Reichert-Meissl value; octoic and decoic acids give both Reichert-Meissl and Polenske values, the Reichert-Meissl value of decoic acid being distinct but very small. Acids from lauric upwards only give Polenske values. Of the insoluble acids decoic and lauric are easily volatile, palmitic and stearic volatile with difficulty, myristic standing midway between the two groups. In the case of palmitic and stearic acids, the amount that passes over is so small that the Polenske value is practically independent of the quantity of acid originally present. With myristic acid, this is only the case if more than 0·06 gram is present. Lauric acid gives a *maximum* Polenske value with 0·3 gram present. In the case of the easily volatile acids, there is a rough proportionality between the Reichert-Meissl and Polenske values and the weight of acid present. The later fractions of the higher acids are only very slowly volatile in steam, but even fractions of a milligram are easily visible in the condensate. The fact that the Polenske value of the higher fatty acids is independent of the weight present is useful in the analysis of mixtures of fatty acids. The work of Dons (A., 1908, ii, 238; 1909, ii, 75) on the estimation of decoic, lauric, and myristic acids in butter by distillation of the fatty acids in steam is described. If 1 gram of mixed fatty acids is distilled in 100 c.c. of steam (measured as water), the partition coefficient of the volatile acids between distillate and condensate is given by $K=(m_1\times100)/m_2$, where $m_1$ is the weight of acids remaining in the flask and $m_2$ the weight distilling over. The partition of the differont acids is unaffected by the other components of the mixture and depends on their volatility under the conditions of distillation and on the proportion present in the mixture. Dons found that if $c_1$ is the quantity reckoned as c.c. ·0 alkali hydroxide volatilising with the first 100 c.c. of water, Ex, where $r$ is the "volatility" and is equal to 0·244, 0·060, (Svens. for decoic, lauric, and myristie acids respectively, and $x$

equals the percentage of the respective acid in the mixture. The partition coefficient is given by $K=(100\times 1-r)/r$. For decoic, lauric, and myristic acids $K$ has the values 138·1, 733·3, and 2640, respectively. The general formula for $r$ is $r=l_2/(Kl_1+l_2)$, where $l_1$ is the weight of the acid phase and $l_2$ that of the condensed steam. From this it follows that the volatility of a fatty acid becomes greater with decrease in $l_1$. This is borne out by Arnold's experiments. If a series of distillations of a given weight of fatty acid is undertaken, using each time 100 c.c. of aqueous condensate, the weight of a given acid distilling over at the $n$th distillation is given by $c_n=c_1(1-r)^{n-1}$.

In practice, Dons's method is applied as follows. Using 0·5 gram of fatty acids, the Polenske value ($p_{16}$) of the sixteenth distillation is determined. It is considered that decoic and lauric acids have by this time been completely eliminated from the mixture, so that this value is due only to myristic and the higher acids. The latter have a constant figure of 0·2. Hence $c_{16}$(myristic acid)$=p_{16}-0·2$. Hence $c_1$(myristic acid)$=c_{16}/(1-r)^{15}$, where $r=0·0704$. The percentage of myristic acid is given by $c_1/0·016$. Using 1 gram of fatty acids, 700 c.c. of distillate are then collected and the sum of the Reichert-Meissl and Polenske values for the first six distillations, and the Polenske value ($p_7$) for the seventh distillation obtained. The seventh distillate is free from decoic acid, as it no longer gives a Reichert-Meissl value; $p_7-0·2$ is therefore due entirely to lauric and myristic acids, $c_1$ for myristic acid is known, so $c_7=c_1(1-r)^6$. Hence the lauric acid in the seventh distillate is given by $p_7-0·2-c_7$ and from this $c_1$ (lauric) and the percentage of lauric acid in the mixture can be calculated. The percentage of decoic acid can be obtained in a similar manner from the results of the first six distillations. Dons's method is interesting from a theoretical point of view, but cannot be considered established as a practical method of analysing fatty acid mixtures. H. C. R.

**A Micro-extraction Apparatus.** FRITZ LAQUER (*Z. physiol. Chem.*, 1922, **118**, 215—217).—An adaptation of an extraction apparatus for the detection of small quantities of lactic acid of the order 2—10 mg. in tissues. S. S. Z.

**Estimation of Oxalic Acid in Urine.** E. MISLOWITZER (*Biochem. Z.*, 1921, **126**, 77—81).—A comparison has been made of the old standard method of Salkowski and the new calcium acetate process of Bau (A., 1921, ii, 356) for the estimation of oxalic acid in urine. Bau's process was found inferior and especially so if more ether be used for the extraction of the oxalic acid and the extraction be carried out mechanically. H. K.

**The Relation between the Refractive Index and the Chemical Characteristics of Oils and Fats (Glycerides).** G. F. PICKERING and G. E. COWLISHAW (*J. Soc. Chem. Ind.*, 1922, **41**, 74—77T).—An attempt has been made to discover a quantitative relation between the refractive index and the molecular weight, free fatty

acid content, and iodine value of the following oils: linseed, soja bean, cotton-seed, ground nut, palm-kernel, and coco-nut. The *refractive index of each of these oils can be calculated with a high* degree of accuracy from the formula $n_D^{40°} = 1{\cdot}4643 - 0{\cdot}000066(S.V.) - 0{\cdot}0096(A.V./S.V.) + 0{\cdot}000117(I.V.)$ where $S.V.$, $A.V.$, and $I.V.$ are the saponification, acid, and iodine values respectively. The equation has a useful application in the commercial analysis of the above oils. E. H. R.

**Use of the "Silver Method" in the Estimation of Acetaldehyde. Its Application in the Estimation of other Aldehydes. A Convenient Method of Accumulation of Aldehyde and other *Volatile Substances from Body Fluids.*** ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **118**, 241—246).—Further details regarding the method described by Stepp and Fricke (this vol., ii, 236). Acetaldehyde can be removed from body-fluids by steam distillation.

S. S. Z.

**The Detection of Aldol in the Urine of Diabetic Patients.** ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **118**, 218—223).—By distilling acid urine from diabetic patients small quantities of crotonaldehyde have been demonstrated in the distillate; possibly *this is derived from the aldol present in the urine.* The "dimedon" method of precipitation was employed. S. S. Z.

**Micro-estimation of Total Acetone in Urine.** HEINRICH LAX (*Biochem. Z.*, 1921, **125**, 262—264).—An apparatus is pictured and a method described, suitable for clinical use, for the estimation of acetone in 2 c.c. of urine in ten minutes. Twenty-five c.c. of water, 2 c.c. of urine, and 3 drops of 80% acetic acid are distilled for four minutes into a second flask containing 2 c.c. of water and 2 drops of concentrated hydrochloric acid. The ammonia is thus *retained and the acetone passes on and is absorbed by 30 c.c. of* water kept at 0°. Ten c.c. of $N/20$-iodine solution are added and 1 c.c. of 33% sodium hydroxide solution and after three minutes the excess of iodine after acidification is titrated with sodium thiosulphate. H. K.

**Estimation of Monobromocamphor.** ELGAR O. EATON (*J. Ind. Eng. Chem.*, 1922, **14**, 24).—A weighed quantity of about 0·2 gram of monobromocamphor is dissolved in alcohol, 50 c.c. of $N/2$ alcoholic potash solution, and 25 c.c. of 0·4% alcoholic silver *nitrate solution are added and the mixture is boiled under a reflux* apparatus for ninety minutes; during the boiling, further quantities 25 c.c. in all) of the alcoholic silver nitrate solution are added rough the reflux apparatus. After cooling, the mixture is diluted h water to 200 c.c., the solution decanted into a beaker, and the uble portion washed by decantation. This dilute alcohol n is boiled for five minutes with the addition of 1 gram of st, filtered, the filtrate acidified with nitric acid, and treated excess of silver nitrate solution; the silver bromide formed d and weighed. The weight of silver bromide found

multiplied by 1·23 gives the corresponding amount of monobromo-camphor. Potassium bromide is formed in the first part of the process, and not silver bromide. W. P. S.

**Extraction and Characterisation of Alkaloids.** W. C. Colledge (*J. S. African Chem. Inst.*, 1922, **5**, 5—8).—A description of methods of purifying extracted alkaloids, methods of testing, general alkaloidal reagents, certain colour reactions, etc. Physiological tests may be applied when any doubt exists as to the nature of a supposed alkaloid. W. P. S.

**Extraction of Alkaloids from Viscera.** W. C. Colledge (*J. S. African Chem. Inst.*, 1922, **5**, 3—5).—The Stas-Otto method is recommended; substances produced by putrefactive changes and extracted together with the alkaloids do not interfere with the identification of the latter, but if desired, the alkaloidal residue may be purified by dissolving it in a mixture of benzene and amyl alcohol, shaking the solution with dilute hydrochloric acid, separating the acid aqueous layer, extracting this with light petroleum, and then rendering the solution alkaline and extracting it with ether. For the detection of morphine, the alkaloidal residue is dissolved in acetic acid, the solution treated with lead acetate to precipitate meconic acid, and the morphine is extracted subsequently from the ammoniacal solution by means of amyl alcohol. In some cases, dialysis of the original material (stomach contents, etc.) affords a means of separating certain alkaloids such as strychnine and morphine. W. P. S.

**Iodic Acid as a Microchemical Reagent for the Detection of Organic Bases.** L. Rosenthaler (*Schweitz. Apoth. Zeit.*, 1921, **59**, 477—479; from *Chem. Zentr.*, 1921, iv, 1055—1056).—The precipitates obtained with iodic acid and solutions of organic bases have in many cases characteristic forms, suitable for use in microchemical work. Strychnine, cinchonine, morphine, codeine, hydrastinine, pyridine, quinoline, and aniline give characteristic crystalline precipitates. Other alkaloids and organic bases may be distinguished by colorations. G. W. R.

**Identification of Alkaloids under the Microscope from the Form of their Picrate Crystals.** Burt E. Nelson and Helen A. Leonard (*J. Amer. Chem. Soc.*, 1922, **44**, 369—373).—The more commonly occurring vegetable alkaloids may be tentatively identified under the microscope by the form or habit of their picrate crystals prepared under standard conditions. A chart is given showing the crystalline structure of the picrates of twenty-five of the alkaloids. For the test, the aqueous solution of the separated alkaloid is slightly acidified with hydrochloric acid and a slight excess of a saturated solution of picric acid is added. The precipitated picrate is washed in a centrifuge and recrystallised from the smallest possible amount of warm 95% alcohol. The crystals are separated centrifugally and examined under a microscope without a cover-slip. W. G.

**Estimation of Carnosine in Muscle Extract.** GEORGE HUNTER (*Biochem. J.*, 1921, **15**, 689—694).—Consistent results can be obtained in the estimation of carnosine in muscle by the diazo-method of Koessler and Hanke (A., 1920, ii, 67). Details are given of the method recommended by the author for preparing the protein-free extract, together with a few analytical results. Ox muscle is found to contain from 0·4% to 0·6% of carnosine. W. O. K.

**Pyrimidines. XCII. New Methods of Identifying the Pyrimidine, Thymine.** TREAT B. JOHNSON and OSKAR BAUDISCH (*J. Amer. Chem. Soc.*, 1921, **43**, 2670—2674).—The thymine molecule is completely destroyed at the ordinary temperature when subjected in aqueous solution to the oxidising action of the system ferrous sulphate plus sodium hydrogen carbonate plus air. The products formed are pyruvic acid, acetylcarbinol, urea, and formic acid. The urea may be identified by its xanthydrol derivative and the formic acid by its reducing action. The pyruvic acid is best identified by its interaction with *o*-nitrobenzaldehyde in alkaline solution to form indigotin. For the detection of acetylcarbinol Baudisch's specific reaction (cf. A., 1918, ii, 412) with *o*-aminobenzaldehyde is best used. Uracil and cytosine are also oxidised by the above reagent, but in neither case is any pyruvic acid obtained and hence the detection of this acid among the products of the oxidation is sufficient proof of the presence of thymine in the original material. W. G.

***Colorimetric Estimation of Uric Acid. Estimation of* 0·03 to 0·5 mg. quantities by a New Method.** J. LUCIEN MORRIS and A. GARRARD MACLEOD (*J. Biol. Chem.*, 1922, **50**, 55—63).—The phosphotungstic acid reagent used by Folin and Denis (A., 1913, ii, 162) is replaced by an arsenotungstic acid reagent which produces a greater depth of colour. Uric acid is precipitated from urine or deproteinised blood by the addition of zinc chloride and sodium carbonate (cf. A., 1916, ii, 456). After separation by centrifuging, it is dissolved in hydrochloric acid and the colour developed in the presence of sodium cyanide by the addition of the arsenotungstic acid reagent compared with a standard. The formation of precipitates is avoided by the use of sodium cyanide as the only alkali. E. S.

***A Modification of Folin's Colorimetric Method* for the Estimation of Uric Acid.** HENRY JACKSON, jun., and WALTER W. PALMER (*J. Biol. Chem.*, 1922, **50**, 89—101).—The estimation is made by the method of Folin and Denis (A., 1913, ii, 162), using a modified phosphotungstic acid reagent. The addition of sodium carbonate is omitted, the necessary alkalinity being furnished by the use of sodium cyanide. By these modifications a greater intensity of colour is obtained and the formation of precipitates avoided. E. S.

## General and Physical Chemistry.

**A Modified Form of Double Slit Spectrophotometer.** A. L. NARAYAN and G. SUBRAHMANYAM (*Phil. Mag.*, 1922, [vi], **43**, 662—663).—This consists essentially of an electromagnetically maintained pendulum carrying a double slit, which is mounted in front of the collimator slit of the spectrograph. This form of spectrophotometer is free from the defects of Vierordt's type, giving a better method of regulating the brightness of the spectrum. It also possesses many of the advantages of the sector photometer.

W. E. G.

**Molecular Refraction of some Molten Salts.** G. MEYER and ADOLF HECK (*Z. physikal. Chem.*, 1922, **100**, 316—333; cf. this vol., ii, 241).—The index of refraction of molten sodium nitrate, potassium nitrate, sodium hydroxide, and potassium hydroxide has been determined by the method of autocollimation at a series of temperatures between 320° and 440°. The following values of the refractive index are recorded: sodium nitrate, 643·9$\mu\mu$, $n$=1·479—1·75$\times10^{-4}t$; 589·3$\mu\mu$, $n$=1·499—2·12$\times10^{-4}t$; 579·1$\mu\mu$, $n$=1·487—1·75$\times10^{-4}t$; 546·1$\mu\mu$, $n$=1·483—1·50$\times10^{-4}t$; potassium nitrate, 643·9$\mu\mu$, $n$=1·525—3·12$\times10^{-4}t$; 589·3$\mu\mu$, $n$=1·664—4·00$\times10^{-4}t$; 579·1$\mu\mu$, $n$=1·556—5·75$\times10^{-4}t$; 546·1$\mu\mu$, $n$=1·538—3·12$\times10^{-4}t$; sodium hydroxide, 643·9$\mu\mu$, $n$=1·467—1·25$\times10^{-4}t$; 589·3$\mu\mu$, $n$=1·458—8·75+$10^{-5}t$; 585·7$\mu\mu$, $n$=1·460—8·75$\times10^{-5}t$; 558·9$\mu\mu$, $n$=1·471—1·12$\times10^{-4}t$; potassium hydroxide, 643·9$\mu\mu$, $n$=1·453—1·0$\times10^{-4}t$; 589·3$\mu\mu$, $n$=1·479—1·5$\times10^{-4}t$; 585·7$\mu\mu$, $n$=1·479—1·33$\times10^{-4}t$; 558·9$\mu\mu$, $n$=1·475—1·33$\times10^{-4}t$. The density of molten sodium hydroxide and potassium hydroxide has been determined and the following values have been found: sodium hydroxide, 340°, 1·89; 400°, 1·86; 440°, 1·84; potassium hydroxide, 380°, 1·87; 420°, 1·83, and 440°, 1·81. The molecular refractivity calculated according to the formula $(n^2-1).M/(n^2+2).d$ is in all cases in keeping with the theoretical value. In the case of sodium nitrate, the degree of dissociation has been calculated from the molecular refraction and shown to be 64·7%.

J. F. S.

**A New Band Spectrum of Oxygen.** C. RUNGE (*Physica*, 1921, **1**, 254—261).—A direct current, high voltage arc was operated in a cylinder through which a stream of oxygen was passed, and a group of bands photographed in the region λ 2200—4900 Å. Although closely crowded towards the ends of the region, the separate lines could be observed from λ 2980 to λ 3900. The vibration frequencies are given by an expression of the form $a+bn+cn^2$; for the first series, $n$ is a whole number, and for the related series, negative fractional numbers differing by whole numbers. Formulæ representing seven bands are given.

CHEMICAL ABSTRACTS.

**Structure of the Band Spectrum of Helium.** W. E. CURTIS (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 38—64). An investigation of the structure of the red band near λ 6400, the green band near λ 5730, and a blue band near λ 4550 in the helium spectrum. The principal features of the structure are shown to be accounted for by the quantum theory of band spectra, which are considered to originate in the passage of molecules between stationary states characterised by constant values of angular momentum, such passage being possibly accompanied by a change in the configuration of the molecule, as assumed by Schwarzschild. A brief résumé of the theory is given. In each of the three bands a new type of series is found, which, although closely related to the others, has not yet received a theoretical explanation. Certain other departures from the theory are also noted. It is concluded that the spectrum is due to an unstable helium molecule having a moment of inertia equal to about $1 \cdot 8 \times 10^{-40}$ gram cm$^2$. J. S. G. T.

**The Spectra of Helium, Hydrogen, and Carbon in the Extreme Ultra-violet.** J. C. MCLENNAN and P. A. PETRIE (*Trans. Roy. Soc. Canada*, 1921, **15**, iii, 15—25).—In identifying the wave-lengths obtained in vacuum grating spectra of helium, and possibly of hydrogen, regard must be paid to the possibility of certain of the recorded wave-lengths originating in carbon or mercury introduced into the discharge tube. The authors support the contention of Millikan (*Astrophys. J.*, 1920, **52**, 47) that certain of the lines obtained by Lyman (A., 1920, ii, 207) in the Schumann spectrum of helium are due to carbon. In particular, the wave-lengths λλ 1931, 1657, and 1561 Å., together with others of less intensity, originate in the atoms of carbon. The series of wave-lengths the frequencies of which are given by $\nu = 4N(1/2^2 - 1/n^2)$ exists for the spark spectrum in helium. J. S. G. T.

**The Corpuscular Spectra of the Elements.** MAURICE DE BROGLIE (*Compt. rend.*, 1922, **174**, 939—941; cf. A., 1921, ii, 232, 292, 615).—The spectra of the four elements silver, tin, gold, and uranium are given, showing the position of the lines which appear on the photographic plate. To identify the origin of the rays, a selective screen which will absorb certain radiations more strongly than others may be interposed between the source of the *X*-rays and the apparatus. Thus a screen containing the oxides of the rarer earths causes the almost complete disappearance of the β- and γ-rays of the *K* spectrum of tungsten. W. G.

**A New Method of Absorption Spectroscopy.** WALTER GERLACH and ERICH KOCH (*Ber.*, 1922, **55**, [*B*], 695—697).—The sources of light usual in spectroscopy suffer under the drawback that they are either insufficiently intense or not so constant as desirable. The defect can be overcome by using as source of light a wire which suffers disintegration by a high-tension condensed discharge. A battery of Leyden jars (capacity about 30,000 cm.) is connected with a spark gap of constant dimensions and the iron wire which is to be disintegrated (about 2 cm. long and 0·031 mm.

ameter). The battery is slowly charged from a small machine ıtil an arc is struck across the gap, when the wire is disintegrated ith a blinding light and the current is broken; a single discharge invariably sufficient for spectroscopic purposes. The constant ·ightness of the source of light is guaranteed by the constant ıergy expended in producing it, which depends only on the mensions of the spark gap and the thickness of the wire.

The disposition of the apparatus and the methods for its ljustment are fully described and figured in the original. H. W.

**The Absorption Spectrum of Liquid and Gaseous Oxygen.** '. W. Shaver (*Trans. Roy. Soc. Canada*, 1921, **15**, iii, 7—14).—The ›sorption spectra of oxygen, liquid and gaseous, were determined ƴ means of a quartz spectrograph, employing a spark between uminium electrodes under water as the light source. In the visible gion, eight absorption bands were observed in the case of liquid :ygen, and seven with gaseous oxygen. The mean wave-lengths of e bands in the former case were 6285, 5800, 5350, 4816, 4458, ;28, 3631, and 3461 Å. In the case of gaseous oxygen at 140 mospheres pressure, the band at 4458 Å. was absent. At 107 mospheres pressure, the bands at 6285, 5800, and 4816 Å. alone ›re observed. In the ultra-violet, four broad bands, about ı Å. wide, were observed in the case of both liquid and gaseous :ygen. In the former case, the centres of the bands were located 2795, 2731, 2681, and 2631 Å., and each band consisted of a ıe set of symmetrical triplet bands. In the gaseous spectrum, e similar bands observed were slightly displaced towards the tra-violet. It was shown that the bands were not due to the ·esence of nitrogen or ozone. J. S. G. T.

**An Absorption Band Spectrum for Water in the Region Wave-lengths of Several Decimetres.** Richard Weich-ınn (*Ann. Physik*, [iv], **66**, 501—545).—A more detailed account work previously published (this vol., ii, 5).

**Studies in Catalysis. XV. Absorption Spectra of Tri-hylsulphonium Bromide in Various Solvents, in the Short ıfra-red Region.** Henry Austin Taylor and William 'udmore McCullagh Lewis (T., 1922, **121**, 665—675).

**Absorption Spectrum of Benzene Vapour and the Funda-nental Magnitudes of the Benzene Molecule.** Victor Henri Compt. rend., 1922, **174**, 809—812).—The ultra-violet absorption pectrum of benzene vapour is composed of four series of super-›osed bands, which obey the formulæ, $1/\lambda=37703+921\cdot4n-159p+2p^2)+2(m^2-q^2)$; $1/\lambda=37494+921\cdot4n-(159p+2p^2)+2(m^2-q^2)$; $1/\lambda=37613+921\cdot4n-(159p+2p^2)+2(m^2-q^2)$; $1/\lambda=37426+921\cdot4n-166p+2(m^2-q^2)$, where $n$ has the values 0 to 7, $p$ the 'alues 0 to 6, and $q=m$ or $q=m\pm1$ and $m=1, 2 \ldots 10$. Eight roups of bands correspond with the eight values of $n$. The posi-ions of the heads of the bands in each group correspond with the ifferent values of $p$, and the values of $m$ give the fine structure of

each band. The intensity of the bands diminishes rapidly as $p$ increases. The constants 921·4 and 159 represent the number of vibrations of the atomic nuclei or of the groups of atoms in the molecule. Hence the infra-red absorption spectrum is given by $1/\lambda=921{\cdot}4n-159p$, and this is confirmed by the results of Coblentz and Puccianti. The moment of inertia of the benzene molecule is deduced as being $1{\cdot}45\times10^{-38}$. From this the distance between the carbon atoms is calculated as being $1{\cdot}85\times10^{-8}$ cm. and the diameter of the molecule as $2{\cdot}6\times10^{-8}$. Thus the benzene molecule is a very symmetrical edifice the movements of which obey the simple laws deduced for diatomic molecules, and it may be considered as being formed of two halves, $C_3H_3$-$C_3H_3$, which vibrate with respect to one another. W. G.

**Ultra-violet Absorption Spectrum of Phenol in Different Solvents.** F. W. KLINGSTEDT (*Compt. rend.*, 1922, **174**, 812—815).—A quantitative study of the ultra-violet absorption spectrum of phenol in different solvents shows that the spectrum of phenol dissolved in pentane or hexane, which the author calls the normal spectrum, comprises two regions in the ultra-violet. In the first, between $\lambda=2860$ and 2400 there are three intense narrow bands, and in the second, between $\lambda=2325$ and the extreme ultra-violet there are two broad bands. The absorption spectrum changes with the nature of the solvent, and from this point of view the solvents may be divided into two groups. The solvents of the first group, such as carbon tetrachloride, chloroform, ether, do not modify the general aspect of the absorption spectrum, only producing a displacement and a broadening of the bands. The solvents of the second group, such as methyl or ethyl alcohol or water, completely modify the absorption spectrum of phenol. In these solvents there is only a single very broad and uniform band. The absorption spectrum of pure liquid and solid phenol occupies a position intermediate between the two preceding types. W. G.

**Fundamental Laws of Photochemistry. II. Influence of Cooling on the Absorption of Light by Dyes.** P. LASAREV (*Z. physikal. Chem.*, 1922, **100**, 266—270; cf. this vol., ii, 103).—The absorption of light of wave-lengths $\lambda=514$, 543, 559, 576, 595, 617, and 644 by layers of collodion containing cyanin and pinacyanol has been measured at ordinary temperatures and at the temperature of liquid air. In the case of cyanin, it is shown that the simple absorption band becomes narrower, whilst in the case of pinacyanol the single band is resolved into two absorption bands at the temperature of liquid air. J. F. S.

**Application of Photo-electric Cells to the Measurement of the Light Absorption in Solutions. II.** H. VON HALBAN and K. SIEDENTOPF (*Z. physikal. Chem.*, 1922, **100**, 208—230; A., 1921, ii, 145).—An arrangement for measuring the absorption light by solutions is described, which depends on the use of o-electric cells and in which variations in the intensity of ation of a mercury lamp are eliminated by compensation

with two photo-electric cells. The cells are used only as a zero instrument. A rotating sector and a grey wedge are used to measure the weakening of the light. The greatest variation of an individual measurement of the absolute value of the extinction coefficient from the mean value does not exceed 0·5%. Measurements with the wedge permit of the identity of two objects in respect of their light absorption being established to 0·1% and differences can also be determined with the same accuracy. Measurements are recorded for solutions of potassium chromate in potassium hydroxide, equimolecular quantities of potassium chromate and copper sulphate in ammonia, azobenzene in alcohol, and anthracene in alcohol for the mercury lines 579 $\mu\mu$ and 254 $\mu\mu$. J. F. S.

**Colour and Chemical Constitution. XIII. Calculation of the Colour of Monocyclic Dyes.** JAMES MOIR (*Trans. Roy. Soc. Sth. Africa*, 1921, **10**, 35—39; cf. A., 1921, ii, 475).—Dyes which contain only one active colour ring do not fit into the scheme previously described (A., 1921, ii, 6) for those containing two such rings, but their colours are deducible by a similar factorial scheme, based on *p*-hydroxybenzyl alcohol (for which, and probably also for *p*-cresol, in faintly alkaline aqueous solution, $\lambda=290$). The factors in parenthesis are employed in conjunction with this value: replacement of carbinol hydrogen by phenyl (1·135); conversion of phenyl carbinol into a phthalein (1·060); replacement of ring hydroxyl- by amino-group (1·140); replacement of amino-hydrogen atoms by methyl (1·035). Values are thus predicted for certain compounds for which measurements are at present lacking. It appears that colour cannot be traced to lower terms than the presence of one benzene ring, with one ionisable group, usually with another active atom, and that the physical cause of colour is the periodic motion of an electron round a molecule. Although the sinuous orbit previously conceived (A., 1921, ii, 475) is now considered not to be very likely, the tautomeric pauses then assumed are a probable feature of the orbit. It is suggested that the colours of dyes containing two active colour rings (*loc. cit.*) may be based on 4 : 4′-dihydroxybenzhydrol ($\lambda=539$). The pink colours attributed to phenylphenolphthalein and to its analogue from salicylic acid (A., 1917, ii, 349; 1919, ii, 78) were due to impurity. J. K.

**Constitution and Colour. VIII.** F. KEHRMANN (*Helv. Chim. Acta*, 1922, **5**, 158—163; cf. A., 1921, ii, 476).—The effect of salt formation on the colour of basic nitrogen compounds is to lighten it if the unsaturated condition is destroyed, and to intensify it if the unsaturated condition persists (for example, in the cases of auramine base, azo-compounds, azomethines, and members of the quinoline, pyridine, acridine, phenazine, etc., series). If no change occurs in the degree of saturation (for example, ammonium, onium, cyclonium, and diazonium compounds), the colour is also unchanged. Similar generalisations apply to basic sulphur and oxygen compounds, with the reservation that knowledge of the colour changes accompanying destruction of the unsaturated con-

dition in these cases is at present insufficiently specific. The behaviour of the group, ·CH:CH·, is apparently analogous to that of the azo-group, since intensely coloured sulphates of diphenyl*cyclo*pentadiene (Borsche and Menz, A., 1908, i, 147) and of unsaturated ketones (Kehrmann and Effront, A., 1921, i, 348) have been described. The effect of salt formation on the colour of iodonium compounds is so far unknown. The above rules also apply to all those cases of salt formation from pseudo-bases (for example, carbinol bases) in which the nature of the changes is properly understood. J. K.

**Fluorescence and Photochemistry.** R. W. Wood (*Phil. Mag.*, 1922, [vi], **43**, 757—765).—The theory of Perrin (cf. A., 1918, ii, 418) is tested by exposing aqueous solutions of eosin, rhodamine, and fluorescein to a very intense beam of sunlight. The products, "photo compounds," are usually coloured, non-fluorescent substances, which are bleached by further action of the light. Their absorption bands have a totally different form from those of the original substances. Rhodamine is almost non-fluorescent at 100°, but decomposes under the action of light as rapidly as at ordinary temperatures. This is contrary to Perrin's theory. The relation between the rate of breakdown of eosin and the intensity of the light is at variance with the Bunsen-Roscoe law, whereas unstable non-fluorescent substances behave normally. The proportionality between the emission of fluorescence and the intensity of the exciting light holds over a wide range of intensity. W. E. G.

**The Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose, Sugars, and other Substances.** Samuel Judd Lewis (*J. Soc. Dyers and Col.*, 1922, **38**, 68—76, 99—108).—An instrument has been designed by which the fluorescent powers of different substances can be quantitatively compared. It consists of a Hilger quartz spectrograph with the back of its camera modified so as to accommodate the lens of an auxiliary camera of the ordinary type directed towards the position usually occupied by the photographic plate of the spectrograph. The usual spectrum falls on to the paper, fabric, or other substance placed in the position of the photographic plate of the spectrograph. The auxiliary camera is directed on to the ultraviolet region only, and since the lens is of glass, any light transmitted by it must consist of visible light produced from the ultraviolet light by the fluorescent substance under examination. As a standard for comparison, Whatman No. 44 filter-papers were used and quantitative comparison was obtained by comparing the times required by the standard and the substance under examination to produce equal photographic effects in a given part of the spectrum. Great difficulties were met in obtaining suitably sensitive photographic plates, and it is suggested that the properties of gelatin may vary with the season of the year at which it is prepared. This method of investigation was applied to determine the fluorescent properties of many different textiles and woods, of papers made from pure cotton, flax, hemp, esparto, and ramie, of cellulose

derivatives, and of a number of carbohydrates, including several sugars, starch, and dextrin. The results are presented in the form of curves in which the fluorescence, expressed as a percentage of that of the arbitrary standard, is plotted against the wave-length of the incident light. Cellulose acetate was the most strongly fluorescent of the cellulose derivatives examined, the maximum strength being at λ 2500—2800, where it was seven times that of the standard. Cellulose nitrate is almost devoid of fluorescent properties. The sugars examined included xylose, dextrose, galactose, lævulose, sucrose, maltose, and lactose, and indications were found of some relation between structure and fluorescent power. There is some evidence to suggest that the cellulose complex may contain groups more nearly related to dextrose than to *d*-fructose. E. H. R.

**The Spectra Structure of the Luminescence excited by the Hydrogen Flame.** HORACE L. HOWES (*Physical Rev.*, 1921, **17**, 469—474).—An investigation, with determinations of wave-lengths, of the spectra of the luminescence of air-slaked lime, and of certain phosphorescent sulphides ("strontium sulphide–bismuth sodium sulphate," "strontium sulphide–bismuth potassium phosphate," and a calcium sulphide compound containing both bismuth and fluorine as active elements), when partly bathed in a hydrogen flame, but at a temperature below red heat. A. A. E.

**Scattering of Light by Dust Free Liquids. II.** W. H. MARTIN and S. LEHRMAN (*J. Physical Chem.*, 1922, **26**, 75—88).—A continuation of previously published work (A., 1920, ii, 573). In the present paper, the relative intensity and polarisation of the light scattered by dust-free benzene, toluene, xylene, chlorobenzene, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, water, and mixtures of carbon disulphide with ether, benzene with hexane, and hexane with *cyclo*hexane have been measured with an accuracy greater than that obtained in earlier work. The increased accuracy was made possible by the use of cross-shaped containers with sealed in, flat, glass end plates in place of the bulbs used previously. Measurements of the light scattered by two-component liquid solutions show that the relative intensity of the scattered light is always somewhat greater than that calculated on the assumption that the scattered light is an additive property for the two liquids. Liquids which polarise the scattered light very far from completely show, on dilution, much more nearly complete polarisation. Measurements of the ratio of the intensity of incident light to that of scattered light have been made for liquids. The results show that ether and water scatter about one-tenth as much light as do the same weights of these liquids in the gaseous state. For benzene and its homologues, the ratio is about one-fifth. Measurements of the intensity of the scattered light for various wave-lengths show that this value varies inversely as the fourth power of the wave-length. J. F. S.

**Radiation and Chemical Action.** T. W. J. TAYLOR (*Nature*, 1921, **108**, 210; cf. following abstract).—An experimental refutation of Lewis's explanation that the velocity of inversion of sucrose by dilute acid is not increased by sunlight because the activating rays lie in the region of $1\mu$, and at this wave-length water would absorb the radiation almost totally in the first thin layer, so that the bulk of the liquid would remain unaffected (cf. Lindemann, A., 1920, ii, 743). A solution of sucrose containing hydrogen chloride was forced upwards in bright sunlight through extremely fine capillary jets; the liquid formed fine columns about 8 cm. high, which then broke up into clouds of small drops (about 0·015 cm. in diameter), the drops rising a further 40 cm. After falling during an average time of 0·68 second, the drops were collected. The rotation was only 0·24° less than that of an unexposed control portion of the solution. Even assuming that the radiation density at $1\mu$ had been reduced, by absorption, inside each drop to $10^{-8}$ of its value, which is considered to be unlikely, a difference in polarimeter readings of about 13° would have been anticipated. A. A. E.

**Radiation and Chemical Action.** W. C. McC. LEWIS (*Nature*, 1921, **108**, 241; cf. preceding abstract.).—An alternative reply to Lindemann's criticism (A., 1920, ii, 743) of the radiation hypothesis of chemical reactions, based on the relatively small absorption capacity of the reactant solutes (cf. Lewis and McKeown, A., 1921, ii, 623). A clear distinction must be drawn between photochemical and thermal conditions, the former involving an absorption coefficient term. It is argued mathematically that the photochemical fractional decomposition and the thermal value (about 0·01 of the magnitude of the former) would be inappreciably small in Taylor's experiments. Further, Taylor carried out no determination of the amount of radiation absorbed by the sugar in the solution; if this were small, no chemical change in excess of the thermal change would be anticipated. A. A. E.

**Dependence of Velocity of Reaction on the Concentration in Photochemical Processes.** M. VOLMER and K. RIGGERT (*Z. physikal. Chem.*, 1922, **100**, 502—511).—The velocity of the dissociation of anthracene in hexane solution into a positive residue and an electron has been determined with the object of testing Luther and Weigert's (A., 1905, ii, 785) expression for the dependence of the velocity of photo-decomposition on the concentration. The expression has the form $v = dC/dt = kJ_0(1 - e^{-\epsilon Cd})/d$, where $C$ is the concentration, $\epsilon$ the extinction coefficient, $d$ the thickness of the illuminated layer, $J_0$ the intensity of the light, and $k$ a constant. The amount of change was measured by the saturation current. It is shown that the current experimentally observed and that calculated from the above-mentioned equation are in excellent agreement, thus proving the correctness of the formula. J. F. S.

**Theory of Induced Reactions.** CHR. WINTHER (*Z. physikal. Chem.*, 1922, **100**, 566—571).—A theory of induced reactions is

put forward which is based on the conversion of oxygen into ozone in the presence of zinc oxide by ultra-violet light and other induced reactions. In the case mentioned, it is assumed that the light is absorbed by the zinc oxide and the light energy is given out again in the form of very short wave-length radiation which is photochemically absorbed by the oxygen. J. F. S.

**The Action of Light on Silver Bromide.** ERNST JOHANNES HARTUNG (T., 1922, **121**, 682—691).

**Action of Light on Uranium Salts.** J. ALOY and E. RODIER (*Bull. Soc. chim.*, 1922, iv, **31**, 246—249).—Under the influence of light, uranyl salts are converted into uranous salts in the presence of the acid entering into the constitution of the salt and a readily oxidisable substance such as alcohol. The reaction which occurs is as follows:

$$UO_2Cl_2 + 2HCl + C_2H_5{\cdot}OH = UCl_4 + CH_3{\cdot}CHO + 2H_2O.$$

Two molecules of acid are necessary for each molecule of uranyl salt. In this way, the fluoride, chloride, bromide, iodide, and sulphate have been prepared, and an aqueous solution of the nitrate. If an insufficient amount of acid is present, basic salts are obtained. If the reaction is allowed to proceed further, a black precipitate of uranous hydroxide is obtained. W. G.

**Photolysis of Uranyl Oxalate and Uranyl Acetate.** EMIL BAUR and A. REBMANN (*Helv. Chim. Acta*, 1922, **5**, 221—239).—If photolysis consists of two processes respectively akin to anodic oxidation and cathodic reduction, the presence of a suitable third substance should affect the quantitative, and possibly the qualitative, results of the process. Thus, the photolysis of oxalic acid by uranyl salts accords with the scheme:

$$U^{VI}\begin{cases} \oplus\oplus + HCO{\cdot}CO_2H = CO + CO_2 + 2H^{\cdot} \\ \ominus\ominus + CO_2H{\cdot}CO_2H + 2H^{\cdot} = HCO{\cdot}CO_2H + H_2O, \end{cases}$$

which is supported by the decomposition of glyoxylic acid under similar conditions (A., 1919, ii, 264):

$$U^{VI}\begin{cases} \oplus\oplus + HCO{\cdot}CO_2H = CO + CO_2 + 2H^{\cdot} \\ \ominus\ominus + U^{VI} = U^{IV} \end{cases}.$$

In the latter reaction, no evidence could be obtained of the formation of glycollic acid, or of formaldehyde, derived from its decomposition in the photolysis of uranyl oxalate. On the other hand, the influences of mercuric chloride, potassium iodide, ferrous sulphate, quinol, uranyl chloride, and sodium uranyl oxalate respectively in increasing the proportion of carbon dioxide formed in comparison with carbon monoxide are explicable in accordance with the theory. Sodium sulphite has no effect (compare Hatt, A., 1918, ii, 143; Trümpler, A., 1916, ii, 9), and formic acid only gives rise to excess of carbon dioxide in the later stages of the reaction, probably because the formate- takes place independently of the oxalate-photolysis. The gas produced in the photolysis of uranyl acetate (A., 1918, ii, 143), and considered to be hydrogen, is now shown to have been carbon monoxide originating from glyoxylic acid, frequently present as an impurity in acetic acid. Two reactions occur

during the photolysis of uranyl acetate: (1) true photocatalyt decomposition into methane and carbon dioxide (Fay, A., 1896, 464), (2) non-catalytic oxidation of acetate-ions to ethane a carbon dioxide by uranyl salts, which only occurs in acetic ac solution with a sufficient concentration of acetate-ions. T photolysis is favoured by the presence of free acetic acid, b restricted by chloridions and mercuric-ions to some extent, almc entirely by ferric salts or formic acid. Such a reaction cannot looked on as, for example, a unimolecular decomposition of the uran acetate complex by light, but as an action of the activated uran complex on surrounding molecules by interchange of electror In other words, it is always an oxidation-reduction process, and closely related to electrolysis. Probably Fay's reaction is co nected with Kolbe's electrolytic decomposition of acetates, acet peroxide and atomic hydrogen being the respective anodic a cathodic products, which then interact and form methane a carbon dioxide. Since the photolytic oxidation of acetic acid ethane and carbon dioxide, and of glyoxylic acid to carbon monoxi and carbon dioxide, can be reproduced electrochemically only l the use of a considerable potential difference, it is concluded th the energy quantum absorbed by the uranyl complex must al have such a value as would suffice, not only for the production oxygen, but also for the formation of peroxides. The formati of uranyl peroxide, observed by Usher and Priestley (A., 1906, 881), is recalled in this connection. J. K.

**Photolysis of Uranyl Oxalate.** EMIL BAUR and HAGGE. MACHER (*Z. physikal. Chem.*, 1922, **100**, 36—41).—The action sunlight on aqueous solutions of uranyl sulphate and oxalic acid h been investigated. The products of the reaction are found to l formic acid, carbon dioxide, and carbon monoxide. The amou of formic acid formed is very small, and it is held that it mu remain small because it is used up as fast as it is produced in redu ing the uranyl-ion to uranous-ion. The gas evolved contains slight excess of carbon dioxide above that required for the simp stoicheiometric relationship $CO_2:CO$. The formation of form acid is regarded as a cathodic reduction of carbon dioxide, thus $CO_2 + 2H^{\cdot} + \ominus\ominus = H{\cdot}CO_2H$. J. F. S.

**Action of Ultra-violet Light on Gels.** EDWARD O. HOLME jun., and WALTER A. PATRICK (*J. Physical Chem.*, 1922, **26**, 25—41 —The action of ultra-violet light from an iron arc on silica gel which had been impregnated with acetone, acetic acid, and nitr acid, respectively, and also on celluloid, has been investigated by tensimetric method. The gel was placed in both bulbs of tl tensimeter, and one was exposed to ultra-violet light whilst tl other was kept in the dark and the difference in pressure measure It is shown that the gels give off gaseous products, provided th liquid contained in the gel is decomposed photochemically int gaseous products which are not adsorbed by the gel. Thus increa of pressure was observed in the case of gels containing acetic ac and acetone, but not in the case of nitric acid, for the decompositic

products of nitric acid are strongly adsorbed by silicic acid gel. The gaseous products consist of a mixture of the vapour of the organic liquid itself along with those gases resulting from the photo-chemical decomposition of the liquid. Celluloid behaves in a similar manner under the influence of ultra-violet light. The mechanism of the liberation of the adsorbed liquid is explained as follows. In the gel there are a large number of pores partly filled with the adsorbed substance under great negative pressure and therefore having a very low vapour pressure. The negative pressure in the film is caused by the surface tension acting along the sides of the pores and round their circumference. The force of the surface tension is reduced by the action of ultra-violet light owing to its decomposition of the liquid of the film with the formation of gas bubbles, which prevent the film from completely wetting the surface of the pores, resulting in a decrease of the negative pressure and subsequently an increase in the vapour pressure of the adsorbed substance, and consequent evaporation of some of the liquid. The same mechanism explains the liberation of gases by celluloid under the influence of ultra-violet light, only here the case is complicated by the fact that light decomposes the structure of the gel itself (cellulose nitrate) as well as the solvent in the pores. Hence the reason for celluloid turning brown and becoming brittle under the action of light is evident. J. F. S.

**β-Ray Spectra and their Meaning.** C. D. Ellis (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 1—17).—The shortest wave-length that has hitherto been measured by the crystal method is 0·07 Å.U., which is greater than the wave-lengths of γ-rays emitted by many radioactive substances. A method based on the quantum theory has been developed for the measurement of the wave-lengths of such rays, and has been applied to the cases of the γ-rays of radium-*B*, radium-*C*, and thorium-*D*. The method involves the measurement of the energies of the different lines in the natural β-ray spectrum of the element in question, and the energy of the corresponding line in the excited spectra of a substance of neighbouring atomic number. The numerical results obtained support the view that γ-rays are emitted from the nucleus. The quantum theory is probably applicable to the nucleus, and a part, at least, of the structure of the nucleus is expressible in terms of stationary states. J. S. G. T.

**Coloration and Luminescence produced by the Action of Becquerel Rays.** Stefan Meyer and Karl Przibram (*Z. physikal. Chem.*, 1922, **100**, 334—336).—A number of examples are recorded which show that the coloration, brought about in glass, quartz, and similar materials by exposure to radium rays, may be removed entirely or in part by prolonged heating at comparatively low temperatures. It is also shown that thermoluminescence is exhibited on heating such coloured material at comparatively low temperatures. Thus a piece of colourless glass which has been turned brown by the rays and has remained unchanged for years in daylight on heating at 100° for twenty-four hours became con-

siderably lighter in colour, after several days at 130—140° it showed a violet tinge, and at 150—200° for several days it was definitely violet. Violet coloured glass is more resistant. Quartz which had been coloured brown became colourless after several days' heating at 150—200°. Sapphire which was originally light blue and had become topaz coloured by exposure to radium rays, after heating at 60° for a day became yellow, after a further two days at 80—90° it was pale yellow with a blue tinge, and after several days at 150—200° it regained its blue colour. A piece of kunzite which had become green in colour when heated for nine hours at 90° showed a feeble thermoluminescence, which disappeared in three hour By heating at 170—180°, thermoluminescence was again shown, an the green colour had become much paler in half an hour. Th same piece of material was then slowly heated at 140° withou luminescence appearing, but at 160° weak luminescence appeare which became stronger as the temperature was raised to 185°, an after two hours' heating at 190° the luminescence failed and th kunzite had regained its original lilac colour. J. F. S.

**The Existence of the New Radioactive Element Uranium-' described by Piccard and Stahel.** OTTO HAHN (*Physikal. Z* 1922, **23**, 146—150).—The decrease in activity of a number ( uranium-*X* preparations has been determined to test the observa tions of Piccard and Stahel (A., 1922, ii, 185). The observed activit was the sum of the exponentially decreasing activity of pu uranium-*X* and a constant α activity due to the presence of ioniun No evidence of the existence of uranium-*V* was found. W. E. G.

**Existence of Isotopes of the Disintegration Products ( Actinium and the Meitner Nuclear Model.** MAXIMILIA CAMILLO NEUBURGER (*Z. anorg. Chem.*, 1921, **120**, 150—158).- The actinium family shows many irregularities when compare with the radium and thorium families, which it is suggested a due to the existence of unknown isotopes. The production ( isotopes by branching at radioactinium is probable since th element gives α-particles with two ranges. A scheme is give for the disintegration of radioactinium in which the disintegratio process, α'—β—α—β, is assumed (cf. Meitner, A., 1921, ii, 293). W. E. G.

**Electrochemical Behaviour of Liquid Sodium Amalgams** THEODORE W. RICHARDS and JAMES BRYANT CONANT (*J. Ame Chem. Soc.*, 1922, **44**, 601—611).—A number of improvemen are described in the electrolytic preparation and the subseque manipulation of pure liquid sodium amalgam, as well as in th apparatus for the measurement of the *E.M.F.* of sodium amalga concentration cells with aqueous electrolytes. The *E.M.F.* ( many concentration cells of liquid sodium amalgam has bee measured at 25°, and a few cells also at 15° and 35°. The deviatio of these potentials from the simple concentration law were foun to be greater in sodium amalgam than with any other mercuri 'ution hitherto investigated in detail. The heats of transferen

of sodium from one amalgam to another calculated by the Helmholtz equation are found to be unusually large. J. F. S.

**Solid Thallium Amalgams and the Electrode Potential of Pure Thallium.** THEODORE W. RICHARDS and CHARLES P. SMYTH (*J. Amer. Chem. Soc.*, 1922, **44**, 524—545).—Pure thallium in compact form is definitely shown to possess at 20° an electrode potential 2·1 millivolts higher than saturated thallium amalgam. When immersed in a *N*-solution of thallous-ions and connected with a normal calomel electrode, the total potential 0·6192 is indicated at 25°. The potential of pure thallium is not influenced by quenching the metal, which is so soft that no important strain can exist in it. α-Thallium is the only phase of the pure metal which is stable at ordinary temperatures. Finely divided electrolytic thallium sponge gives a potential 0·6 millivolt higher than the compact fused form. The difference is probably due to the fine state of division, and disappears on long keeping. The difference of potential shown by β-thallium, if it could exist at ordinary temperatures, would probably be nearly three times as great. Solid thallium amalgams may be made having potentials anywhere between that of pure thallium and the 2-phase amalgam. As mercury is added, the potential decreases at first, then remains constant, between 4% and 10% of mercury, and later decreases again until at about 15% of mercury the liquid phase becomes permanent at 20°. Crystals of solid amalgam separated centrifugally from the liquid containing more mercury showed as much as 20% of mercury, but some of this was undoubtedly adhering mother-liquor. The densities of solid thallium amalgams indicate an increase in volume of thallium on amalgamation. The corresponding curve shows a slight inflection at about 5% of mercury. The hardness of solid thallium amalgams increases with added mercury until about 5% is present, when it begins slowly to diminish. From these phenomena it is inferred that α-thallium dissolves mercury, increasing in hardness and volume up to about 5% of mercury. When more mercury is added, another solid phase of about the same hardness and volume, but containing more mercury, appears. These two phases appear to exist mixed together in equilibrium, over the range from about 5% of mercury to 10% at 20°. With more than about 10% of mercury the α-solid solution ceases to exist and the other phase continues to dissolve mercury in solid solution until it is saturated, with perhaps 15% of mercury. The other solid phase is probably a solid solution of mercury in β-thallium, which appears in definite crystalline form, making the amalgam friable after the admixture of α-thallium has been eliminated. β-Thallium can exist at ordinary temperatures only in the presence of much mercury, but it is always the form present in equilibrium with the liquid amalgam. Pure thallium melts at 303·5° and has a transition point at 235·3°. J. F. S.

**Electromotive Behaviour of Aluminium.** ROBERT MÜLLER and FRANZ HÖLZL (*Z. anorg. Chem.*, 1921, **121**, 103—109).—The potential of aluminium and amalgamated aluminium has been

measured in solutions of aluminium chloride, potassium chloride, hydrochloric acid, and sodium hydroxide of various concentrations and in mixtures of hydrochloric acid and aluminium chloride of various concentrations. The values of the potential are fonnd to be in qualitative agreement with the Nernst theory. It is shown, from a comparison of the potentials of pure and amalgamated aluminium in acid and alkaline electrolytes, to be probable that the activation by means of mercury and the apparent anomaly of the potential of pure aluminium is occasioned by a protecting layer of hydroxide. In concentrated hydrochloric acid (6·8 *N*), pure aluminium is more electropositive than the amalgam; cf. Dhar (*ibid.*, 1921, **118**, 75). J. F. S.

**Acidifying Action of Hydroxy-organic Compounds on Boric Acid and Molybdic Acid.** E. RIMBACH and P. LEY (*Z. physikal. Chem.*, 1922, **100**, 393—407).—The authors have measured at 18° the hydrogen potential of solutions of boric acid, molybdic acid, glycollic acid, lactic acid, malic acid, citric acid, tartaric acid, propylene glycol, glycerol, mannitol, and dextrose and also mixtures of the two inorganic acids with various concentrations of each of the organic compounds. The hydrogen-ion concentration has been calculated in each case, and the increase in hydrogen-ion concentration occasioned by the mixing. The results are represented by curves and tabulated. The increase in the acidity is attributed to complex formation in which the hydroxyl group is operative. In the case of boric acid, tartaric acid produces a much greater increase than the monohydroxy-acids, whilst in the mixtures of molybdic acid the reverse is the case. Similar results are obtained with the non-acidic hydroxy-compounds. With molybdic acid, glycerol increases the acidity most, whilst mannitol has a smaller action than propylene glycol, but with boric acid, mannitol and dextrose have the most pronounced action, whilst propylene glycol has a greater action than glycerol. J. F. S.

**Thermodynamic and Electrokinetic Potential Difference at the Surface of Two Liquids.** H. FREUNDLICH and A. GYEMANT (*Z. physikal. Chem.*, 1922, **100**, 182—196).—The thermodynamic potential, $\epsilon$, and the electrokinetic potential, $\zeta$, of the liquids phenol, guaiacol, benzonitrile, and aniline against aqueous solutions of a number of electrolytes have been measured. The $\epsilon$-potential was measured by Beutner's method and the $\zeta$-potential determined from the microscopic observations on the velocity of kataphoresis of the liquid drops. The two potentials are shown to be very largely independent of one another, a fact in keeping with the views of Freundlich (*Kolloid Z.*, 1921, **28**, 240). The negatively charged drops are generally discharged and recharged oppositely by the kations, particularly strongly by multivalent kations such as calcium and aluminium, whereas such an effect does not occur in connexion with the $\epsilon$-potential. A certain similarity of action is observed in the case of some organic ions; the ions of basic dyes and the alkaloids have a positive effect on

both potentials, whilst the anions of organic acids have a negative action. Exceptions and great variations in the dimensions of the action are, however, to be observed. The regularities previously published (*loc. cit.*) are confirmed. The partition relationship of the ions is determinative of the $\epsilon$-potential, the organic liquid phase being more strongly positive or negative the more soluble the kation or anion is in the liquid. In the case of the $\zeta$-potential, the adsorption and valency of the kations are responsible for the discharge and positive recharging of the drops; thus, for example, the kations of the basic dyes and the multivalent kations have a particularly strong action. All four liquids are negatively charged towards water in respect of their $\zeta$-potential, even aniline, despite its strongly basic character. J. F. S.

**Measurement of Overvoltage.** HERMAN V. TARTAR and HARMON E. KEYES (*J. Amer. Chem. Soc.*, 1922, **44**, 557—567).—The conclusions of earlier investigators that overvoltage increases with time and current density and varies with the nature of the electrode surface have been confirmed. A comparison, based on the transition point for hydrogen-zinc deposition from solutions containing sulphuric acid and zinc sulphate, has been made by the two methods used for overvoltage measurement. The data obtained show that the commutator method gives erroneous results; when gas is being evolved at the experimental electrode, the error is large and varies with the speed of rotation of the commutator. The direct method has been found to give more consistent results and to be the more accurate method; the criticism that it is subject to variation due to electrode spacing and size and shape of the containing vessel is shown to be invalid. The existence of an appreciable transfer resistance at the surface of the electrodes examined is doubtful. While gas is being evolved, it is evidently not of the magnitude which has been stated. Evidence is advanced which indicates that the ordinary hydrogen overvoltage tables, obtained by using pure acid solutions as electrolyte, do not show the current densities necessary for the deposition from acid solutions of metals having a greater *E.M.F.* than hydrogen. J. F. S.

**Low-voltage Standard Cells.** J. OBLATA (*Proc. Phys. Math. Soc. Japan*, 1921, [iii], **3**, 136—149; cf. *ibid.*, 1921, [iii], **3**, 64).—The properties of various cell combinations were studied in order to obtain a satisfactory low-voltage standard. The following two were the most reproducible and constant: Cd amalgam | $CdI_2$ | $PbI_2$ | Pb amalgam, and Cd amalgam (10%) | $CdSO_4,8/3H_2O$ | Cd amalgam (dilute). The *E.M.F.* of the former is 0·09838 at 20° and that of the latter is of the order of 0·01 volt, giving different values according to the concentration of the dilute amalgam. The temperature coefficients were determined between 15° and 30°. The heats of formation of cadmium chloride, iodide, and bromide were computed by applying the Gibbs-Helmholz equation. They were found to be 94090, 49340, and 74700 cals., respectively.

CHEMICAL ABSTRACTS.

**Modifications of Kohlrausch's Method for the Measurement of the Conductivity of Electrolytes.** MARCEL ABRIBAT (*Bull. Soc. chim.*, 1922, iv, **31**, 241—245).—The ordinary telephone receiver used for determining the zero point on the Wheatstone bridge is replaced by a galvanometer. In order to permit of this, the current passing through the galvanometer is converted from alternating to direct by means of a thermionic valve. The arrangement of the apparatus is sketched. To make the readings still more exact, an amplifier may be used. W. G.

**Questions Relating to the Constitution and Function of Electrolytes.** W. MADELUNG (*Annalen*, 1922, **427**, 35–109).—A theoretical enquiry into the constitutional causes which determine the formation and stability of electrically charged atomic aggregates (ions) in crystals and in solution. The form of the paper does not admit of satisfactory abstraction, and the original should be consulted in order to obtain a just appreciation of the comprehensive character of the author's views.

Hantzsch's theory of $\psi$-isomerism is discussed and extended. The cyanogen compounds described in the preceding paper (cf. this vol., i, 438) are $\psi$-acids in their non-ionisable forms, and true acids in the forms corresponding with their salts: disodium cyanamide is Na·N:C:N·Na, sodium dicyanamide is Na·N:C:N·CN, and sodium cyanoform is Na·N:C:C$(CN)_2$. Corresponding with $\psi$-acids and $\psi$-bases, a class of $\psi$-salts can be recognised as falling within the same view of $\psi$-isomerism. Aluminium and stannic chlorides are not ionised as such; they are therefore $\psi$-salts. In general, the univalent and some bivalent metals tend to form salts, whilst most of the ter- and quadri-valent metals form $\psi$-salts. The sodium compound of acetyl acetone is an electrolyte and non-volatile, like sodium chloride, whilst the aluminium derivative is a non-electrolyte and is volatile, like aluminium chloride; both the sodium compounds are salts, and both the aluminium compounds $\psi$-salts. In order to form ions, the ter- and quadri-valent metals have to combine with other ions or molecules to form centrically orientated complexes: $[Fe(H_2O)_6]^{\cdot\cdot\cdot}$, $[Fe(CN)_6]'''$, $[Cr(NH_3)_6]^{\cdot\cdot\cdot}$, $[SnCl_6]''$.

Ionisation therefore is largely a matter of the formation of centrically orientated complexes. In acids, it is assisted by the accumulation of a number of electro-negative peripheral groups around the nuclear atoms, for example, $[Fe(CN)_6]'''$ and $[SnCl_6]''$. In bases, the accumulation of hydrogen atoms either as such, as amino- or hydroxyl-groups, or as water or ammonia molecules, has a similar effect; cf. $[NH_4]^{\cdot}$, $[PH_4]^{\cdot}$, $[Cr(NH_3)_6]^{\cdot\cdot\cdot}$, etc. Even carbon may become the central atom of an ion if sufficiently loaded with electrically powerful groups; the ion of guanidine is represented by the formula $[C(NH_2)_3]^{\cdot}$, which expresses its strongly basic character much better than the customary formula based on the integral valencies of the organic chemist. *tert.*-Butyl iodide, $(CH_3)_3CI$, is better termed trimethylcarbonium iodide, as it is ionised in solution in liquid sulphur dioxide, a remarkable instance

of the tendency of a large accumulation of hydrogen atoms to promote *ion-formation*; the *ions* $[C(CH_3)_3]^{\cdot}$, $[C(NH_2)_3]^{\cdot}$, and $[CO_3]''$ are strictly analogous.

Apparently simple ions, $H^{\cdot}$, $OH'$, $NO_3'$ are subject to the same laws regarding the tendency to centric orientation and the influence of the peripheral groups. Hydrogen- and hydroxyl-ions are invariably combined with at least one molecule of water: $[OH_3]^{\cdot}$, $[H(OH)_2]'$, and often with more. By assuming a further degree of hydration, chains may be produced which are strongly reminiscent of the structure of the crystalline compound:

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H- & & O & -H- & O & -H- & \end{array}$$

The electrical influence of peripheral groups is often felt, not only in the circumjacent atoms, but also in more remote parts of the molecule. This phenomenon is termed induction; it is fully discussed and illustrated by many examples in the original paper.

C. K. I.

**[Theory of Strong Electrolytes.]** SVANTE ARRHENIUS (*Z. physikal. Chem.*, 1922, **100**, 9—35).—A theoretical paper in which the author discusses the theory of strong electrolytes as put forward by Ghosh (T., 1918, **117**, 449, 627, 707; 1920, **117**, 823, 1390; this vol., ii, 125). The various calculations made by Ghosh in connexion with the dissociation of strong electrolytes and the more complete calculations of Partington (A., 1920, ii, 151) are considered, and in connexion with those of the former author it is shown that they are not always consistent, nor have they always the deep significance which Ghosh places on them. For example, in a comparison of the Arrhenius formula, $i=1+(n-1)\alpha$, with Ghosh's formula, $i=n(1+\frac{1}{3}\log_e\alpha)$, calculations are put forward by Ghosh which indicate the superiority of the second formula. The present author points out that in obtaining values from the second formula values which had been corrected for viscosity are used in the case of salts of the potassium chloride type, but not for those of the calcium chloride type, whilst with the former formula no correction was applied anywhere. The author concludes that could the Ghosh hypothesis be applied it would be a distinct advance on the previous hypotheses, but, unfortunately, it cannot be applied without great modifications.

J. F. S.

**The λ-*V* Curves of Non-aqueous Solutions of Binary Electrolytes.** P. WALDEN (*Z. physikal. Chem.*, 1922, **100**, 512—531).—A theoretical paper in which the influence of the viscosity, dielectric constant, and mobility on the form of the λ-*V* curves is discussed.

J. F. S.

**Dissociation and Hydrolysis Equilibria in Solutions of Salts of Carbonic and Boric Acids.** HEINRICH MENZEL (*Z. physikal. Chem.*, 1922, **100**, 276—317).—From electrometric measurements of mixtures of sodium carbonate and hydrogen carbonate in various concentrations at 18°, the second dissociation constant of carbonic acid has been determined and the value $K_2=6{\cdot}2\times10^{-11}$ found, which agrees well with the value found by Auerbach and

Pick (*Arbt. Kais. Gesundh.*, 1911, **38**, 2). The hydrolysis of sodiu carbonate has been calculated from the results, and the followin values are recorded: 0·2*M*, 1·12%, 0·1*M*, 1·76%, 0·05*M*, 3·0% 0·02*M*, 5·5%, 0·01*M*, 8·3%, and 0·005*M*, 10·65%. The dissociatio constant for boric acid has been determined at 18° by *E.M.*I measurements of solutions of borax and sodium metaborate, an the value $K_B=5·7\times10^{-10}$ obtained. This value is much small than that recorded by Walker (T., 1900, **77**, 17), but is in keepin with the values recorded by Lundberg and Lundén at other ten peratures. Concentrated solutions of borax and metaborate show in consequence of the formation of polyborate ions, a somewha stronger alkalinity than would be expected from the dissociatio and hydrolysis. The degree of hydrolysis of sodium metaborat has been determined, and the following values have been obtained 0·4*M*, 0·50%; 0·2*M*, 0·57%; 0·1*M*, 0·76%; 0·04*M*, 1·22% 0·02*M*, 1·7%, and 0·01*M*, 2·3%. The equilibrium sodium carbonat + borax ⇌ metaborate + bicarbonate has been experimentally ex amined in dilute solutions, and also in two cases for concentrate solutions where the polyborate formation was taken into accoun

J. F. S.

**Calculation of the Second Dissociation Constant of Dibasi Acids from the Hydrogen-ion Concentration.** MARCE DUBOUX (*J. Chim. physique,* 1921, **19**, 179—187).—Two method are given for calculating the second degree of dissociation of dibasi acids, which are applicable to solutions containing 0·01—0·00 gram-mol. per litre. At these concentrations, the determinatio of the hydrogen-ion concentration presents no difficulties. It i shown that Noyes's formula can be rigorously applied only t solutions less concentrated than 0·001 gram-mol./litre. Makin use of known hydrogen-ion concentrations, the following value have been calculated: tartaric acid, $K_2=32\times10^{-6}$ at 25°, $K_2=$ $28·4\times10^{-6}$ at 76°; malic acid, $K_2=4·1\times10^{-6}$ at 100°; succini acid, $K_2=2·5\times10^{-6}$ at 25°, and $K_2=1·5\times10^{-6}$ at 100°. J. F. S.

**Behaviour of the Photo-haloids in a Direct Electric Curren** C. TUBANDT and GERHARD ESCHENHAGEN (*Z. physikal. Chem* 1922, **100**, 489—501).—The effect of passing a direct electri current through photo-haloids has been investigated. It is show that both the synthetic photo-haloids and those which have bee formed by the action of light are simple electrolytic conductors the presence of colloidal metals, whether adsorbed or mechanicall mixed, does not affect the character of the electrical conductivity Metallic silver may be separated electrolytically from strongl illuminated dry silver chloride, and also from synthetic photo chlorides and bromides, but not from photo-iodides even whe these are mixed with large quantities of colloidal silver. Th colloidal silver in synthetic photo-haloids and also that in illuminate silver haloids is unaffected by a direct current, but the silver-ions the case of pure silver haloids, wander uninfluenced by th particles toward the electrode; a displacement of the silve

les is not observed even when the current is allowed to flow olonged periods. J. F. S.

**hodic Deposits from Mixed Solutions of Two Simple llic Salts.** WALTHER HILDEBRANDT CREUTZFELDT (*Z. Chem.*, 1921, **121**, 25—52).—Mixtures of salts of the follow- airs of metals, copper–cadmium, copper–lead, copper–iron, -copper, silver–cadmium, and silver–zinc, have been electro- by various currents and voltages and binary, fine-grained, lline deposits obtained. It is shown that the composition deposit changes continuously with the current density and omposition of the mixture. By changing these factors, a of mixed crystals may be deposited which varies from one constituent to the other constituent. Measurements of the F. of the deposit show that they are readily oxidised, and placed in water they lose the more electropositive constituent ew hours. In order that a deposit of a given concentration l be obtained, it is necessary that the current density should reased with increasing metal concentration in the solution. re vigorous agitation of the solution acts in the same sense increased current density, whilst an increased temperature in the opposite sense. The dependence of the *E.M.F.* of eposit on the composition is considered in connexion with ıann's theory. The partition of both atom types in the olytic deposit is not the normal one observed in mixed crystals molten mixtures, but a completely unordered one. The bility for the unprotected atoms of the electropositive metal en by $\Sigma w = p^{s-1} . q + p^{2s-4} . q^2 + p^{3s-7} . q + \ldots$, in which $p$ is the ular fraction of the less electropositive metal, $q$ that of the opositive metal, and $s-1$ the number of atoms of the less opositive metal necessary to protect one atom of the more opositive metal from the action of reagents. The fraction the nnprotected atoms of the more electropositive metal is by the equation $\alpha = (q - \Sigma w)/q$. The *E.M.F.* is assumed to oportional to the number of unprotected atoms. It is shown the potential–composition curve is determined by a whole er $s$. Four copper atoms are necessary to protect a single ium or lead atom, seven silver atoms are required for a single r atom, and twenty-two copper atoms are necessary to protect gle iron atom. J. F. S.

**termination of the Specific Heat of Solid Substances he Adiabatic Electrical Method.** ERNST COHEN and TH. MOESVELD (*Z. physikal. Chem.*, 1922, **100**, 151—158).— pecific heat of cadmium sulphate has been determined by an atic electrical method previously described (this vol., ii, 156). alorimeter liquid used was bromoform (specific heat 0·1241) hree determinations, using 823 and 676·5 grams respectively of $_4$,8/3$H_2O$, were carried out. The value 0·200 between 17° 21° was obtained, which agrees well with 0·2008 found by ı, Kruisheer, and Moesveld (A., 1921, ii, 156). It is shown

that the values found by Holsboer (0·2225) (A., 1901, ii, 226) and by Seibert, Hulett, and Taylor (A., 1917, ii, 231) are untrustworthy. J. F. S.

**Determination of the Higher Point of Inversion of the Specific Heat of the Saturated Vapour of Benzene.** G. BRUHAT and A. DELAYGUE (*Compt. rend.*, 1922, **174**, 937—939).—Using a Cailletet apparatus with the tube jacketed with glycerol electrically heated, the authors have determined the two points of inversion of the specific heat of the saturated vapour of benzene. The values obtained are 122° and 258° respectively. From a theoretical study of the specific heat of the saturated vapour of benzene, using the characteristic equation for benzene, they obtain the values 121° and 254°. W. G.

**Specific Heats. II.** M. PADOA (*Gazzetta*, 1922, **52**, i, 25—29; cf. this vol., ii, 27).—The views expressed in the former paper lead to the conclusion that the low specific heats of elements deviating markedly from Dulong and Petit's law are due to the high number of valencies used by the atoms to ensure the stability of the crystalline edifice and to the exceptional energy of the corresponding linkings. Thus, if it were possible to separate the atoms of the abnormal element to such an extent that, although participating in the formation of the crystalline network, such atoms were no longer able to exert mutually disturbing actions, their specific heats should increase to the values exhibited by the other elements. Such a condition should be attained in solid solutions of an element of abnormal specific heat in excess of another of normal specific heat. Experimental confirmation of these views is furnished by measurements of the specific heats of silicon–iron and sulphur–selenium mixtures. In the former case, the atomic heat of silicon is 4·74—4·83 in alloys containing 95—50% of silicon, whilst the values for 33·6 (FeSi), 14 and 10% of silicon are, respectively, 5·27, 6·04, and 6·42. Heating of the 10% silicon mixture at above 1000°, followed by rapid cooling, fails to alter the specific heat. In sulphur–selenium mixtures containing 4, 9, 28·77, 90·35 (rhombic), and 90·35 (monoclinic)% of sulphur, the values of the atomic heat of sulphur are respectively 7·03, 6·00, 5·87, 5·50, and 5·78. T. H. P.

**Method of Formation of the Atoms in Carbon Compounds.** HANS BEUTLER (*Z. anorg. Chem.*, 1921, **121**, 67).—In a previous paper (this vol., ii, 259) it was shown that the lattice energy of carbon compounds alternated from member to member. This fact was deduced from the behaviour of the melting point and the heat of combustion of the homologues of aliphatic series. It is now pointed out that the recent work of Becker and Janke (this vol., ii, 128) experimentally confirms the author's hypothesis, since this work shows that the even members of the monocarboxylic aliphatic acids crystallise in the hexagonal and the odd members in the tetragonal system. J. F. S.

**Moment of Inertia and Structure of the Carbon Dioxide Molecule.** A. EUCKEN (*Z. physikal. Chem.*, 1922, **100**, 159—170).—A theoretical paper in which the moment of inertia of the carbon dioxide molecule and its structure are considered. It is shown to be probable that in the molecule of carbon dioxide the carbon atom is situated practically on the line which joins the two oxygen atoms and performs small elastic circular vibrations round these atoms. The moment of inertia vertical to the line joining the oxygen atoms has the value $50 \times 10^{-40}$ $cm^2$. gram, and the mutual distance of the oxygen atoms $2{\cdot}0 \times 10^{-8}$ cm. Carbon dioxide and presumably sulphur dioxide are to be treated thermally as diatomic gases; on this basis the chemical constant $i$ for carbon dioxide has the value 0·80, and the molecular heat at high temperatures, in consequence of the linear vibration of the oxygen atoms and the circular vibrations of the carbon atom, approaches the limiting value $C_{v\infty}=5/2R+4/2R+4/2R=13/2R$. J. F. S.

**Some Relationships between the Critical Temperature and the Melting and Boiling Points.** MAURICE PRUD'HOMME (*J. Chim. physique*, 1921, **19**, 188—189).—The following two relationships are found to hold for the critical temperatnre ($T_c$), the freezing point ($T_f$), and the boiling point ($T_1$) of members of the zero group: $T_1(T_c-T_1)/T_f(T_c-T_f)=1+\epsilon$, where $\epsilon$ is a fraction having a mean value 0·05, and $T_c=(T_f-T_1)(1+\epsilon')$ where $\epsilon'$ has very nearly the same value as $\epsilon$. These formulæ hold for other substances and have been confirmed in sixty different cases.

J. F. S.

**Factors Determining the Hygroscopic Properties of Soluble Substances. I. Vapour Pressures of Saturated Solutions.** GRAHAM EDGAR and W. O. SWAN (*J. Amer. Chem. Soc.*, 1922, **44**, 570—577).—The vapour pressures of saturated aqueous solutions of potassium chloride, potassium nitrate, ammonium chloride, ammonium sulphate, ammonium nitrate, ammonium dihydrogen orthophosphate, sodium nitrate, carbamide, and a mixture of ammonium chloride and potassium nitrate have been measured at temperatures between 20° and 30°. The relationship of the vapour pressures of saturated aqueous solutions to the hygroscopic properties of soluble substances is discussed. The theory relating the vapour pressure of a saturated solution to the temperature and solubility is considered, and on the basis of the Clausius-Clapeyron equation and van't Hoff's equation the expression $\log_e P_1-\log_e P_2=i(S_2-S_1)-Q_1/R(1/T_1-1/T_2)$ is deduced. This equation gives calculated vapour pressures which are in good agreement with those found.

J. F. S.

**The 25°-Isotherms of the Systems Magnesium Nitrate–Sodium Nitrate–Water and Magnesium Sulphate–Magnesium Nitrate–Water.** DOUGLAS NORMAN JACKMAN and AGNES BROWNE (T., 1922, **121**, 694—697).

**Heat of Formation of Compounds of Metallic Magnesium with Metallic Zinc, Cadmium, Aluminium, and Calcium.** WILHELM BILTZ and GEORG HOHORST (*Z. anorg. Chem.*, 1921, **121**, 1—21).—The heat of formation of the intermetallic compounds of magnesium with zinc, cadmium, aluminium, and calcium has been calculated from a series of determinations of the heat of solution of the individual metals and the compounds in hydrochloric acid of various concentrations. The metals were used in the form of fine powders or thin foil, and the solution was hastened by the use of small quantities (about 8 mg.) of a platinum catalyst. The following values of the molecular heat of solution in $HCl,8H_2O$ at 18° are recorded: magnesium, 113·1 Cal.; zinc, 33·55 Cal.; aluminium, 125·1 Cal.; calcium, 130·1 Cal.; cadmium, 19·77 Cal.; $MgZn_2$, 167·6 Cal.; MgCd, 123·7 Cal.; $Mg_4Al_3$, 779 Cal.; and $Mg_4Ca_3$, 800 Cal. The difference between the sum of the heats of solution of the constituent metals and that of the compounds gives the heat of formation of the compounds from the solid metals thus: $Mg+2Zn=MgZn_2+12\cdot6$ Cal.; $Mg+Cd=MgCd+9\cdot2$ Cal.; $4Mg+3Al=Mg_4Al_3+49$ Cal.; and $4Mg+3Ca=Mg_4Ca_3+43$ Cal. The densities of the compounds and that of calcium have been determined and the following values of $d_4^{25^\circ}$ obtained, $MgZn_2$, 5·126; MgCd, 5·383; $Mg_4Al_3$, 2·151; $Mg_4Ca_3$, 1·701; Ca, 1·542. The molecular volumes are calculated and compared with the sum of the atomic volumes, and it is shown that in all cases the compound is formed with a contraction in volume. J. F. S.

**Heat of Reaction of Oxygen with Hæmoglobin.** EDWARD F. ADOLPH and LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1922, **50**, 463—490).—Estimations of the heats of reaction of oxygen and carbon monoxide with hæmoglobin at 22° gave average values of 6,950 and 14,700 cal., respectively. The individual values, however, showed large variations, the extreme values for oxygen being 1,500 and 10,900 cal. and those for carbon monoxide 8,300 and 25,200 cal., although the same apparatus gave consistent results when used for inorganic reactions. The authors conclude from their own results and from those of others that *K* and *Q* for oxyhæmoglobin are not related by the van't Hoff isochore, and discuss various factors which may account for this. E. S.

**Adhesion Forces in Solutions. II. Adhesion Series.** NIKOLAI SCHILOV, NAD. BULYGINA, NIK. ZEREVTINOV, LIDIE LEPIN, OLGA MICHAJLOVA, MICH. DUBININ, SERG. WOSNESSENSKI, AGNESS IVANITZKAJA, LIDIE ORLOVA, and JOH. SASLAVSKY (*Z. physikal. Chem.*, 1922, **100**, 425—462; cf. A., 1920, ii, 591).—In an earlier paper (*loc. cit.*) it was shown that the adsorption of a series of salts of the same anion by charcoal increases with increasing valency of the kation; such a series is termed "convalent." A series of acids under the same treatment gave decreased adsorption with increasing valency of the anion; such a series is termed "antivalent." A series where the univalent ions come at one end, the bivalent at the other, and the tervalent between or irregu-

larly among the uni- and bi-valent ions is termed a mixed series. A number of adsorption experiments have been carried out on the adsorption of electrolytes by alumina, ferric oxide, manganese dioxide, peat, wool, and finely divided metals. The results show in the case of alumina that the adsorption series for acids and for copper salts are both convalent, with ferric oxide and acids the adsorption series is also convalent; manganese dioxide, acids, and copper salts all give convalent series. Peat gives an antivalent adsorption series with acids. In the case of finely divided metals, the adsorption of copper salts by tungsten and antimony is antivalent but by nickel salts convalent. The work with finely-divided metals was rendered difficult owing to chemical action occurring between the two phases; it is shown that an adsorption always precedes a chemical action. Thus iron powder was kept in contact with silver nitrate and it was found that for one hundred and fifty minutes silver was removed from solution to the extent of 3—8% without iron passing into solution, but once the chemical action commenced it proceeded very rapidly to completion. The adsorption of a series of chlorides by wool is convalent. Coagulation series have been investigated for the action of electrolytes on mastic sols, colloidal ferric hydroxide, arsenic sulphide, antimony sulphide, manganese dioxide, and for suspensions of charcoal in alkalis, and in tanuic acid, and iron oxide in $N/50$-hydrochloric acid. The coagulation series of mastic sols is antivalent for acids and for copper salts, but for sulphates it is convalent, although the hydrogen-ion falls among the multivalent ions. The nitrates and chlorides both formed mixed series. With positively charged ferric hydroxide sols, the anion series is convalent, in the case of the acids, copper salts, and potassium salts, whilst the kations all formed mixed series. Arsenic sulphide and antimony sulphide both give an antivalent series for the anions and a convalent series for the kations, whilst manganese dioxide gives an antivalent series for anions and a mixed series for kations. The electrode potential of metals in acids has been divided into similar series, and from the measurements of Ostwald (*ibid.*, 1887, i, 583) it is shown that zinc, cadmium, tin, lead, iron, and antimony give convalent series, mercury and copper antivalent series, and silver and bismuth mixed series. From the work of other investigators it is shown that the influence of anions on the solubility, compressibility of solutions, and the abnormal elevation of the boiling point is convalent, whilst the influence of anions in acid solution on the rate of hydrolysis of esters is antivalent, but in alkaline solution convalent. A calculation of the molecular contraction in the formation of solid chlorides and sulphates gives rise in both cases to convalent series. The experimental results are discussed, and it is shown that the series is due to the processes being controlled by molecular forces rather than by ionic forces. Such molecular forces are termed "cohesion forces" where similar molecules are concerned, and "adhesion forces" where dissimilar molecules participate. J. F. S.

**Validity of the Laws of the Internal Friction of Liqui** W. HERZ (*Z. anorg. Chem.*, 1921, **121**, 95—98).—A theoreti paper in which the author examines the formulæ put forw by Bingham and Harrison (A., 1918, ii, 382) and Batschinski ( *1913*, ii, *928*) to represent the fluidity of the benzene haloi Extrapolating to the absolute zero leads to negative values the fluidity, and from this the author concludes that the fluid is not a strict linear function of either the temperature or t specific volume. J. F. S.

**The Viscosities of some Hydrocarbons.** G. CHAVANNE a (MLLE) H. VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1922, **31**, 87 94; cf. Bartoli and Stracciati, A., 1886, 215; also Thorpe a Rodger, T., 1897, 360).—Viscosity measurements of some hyd carbons lead to the following conclusions: Viscosity increa directly with the number of side chains, for example, 2 : 2 : 3 : tetramethylbutane is a solid; high viscosity is thus condition by the presence of tertiary butyl groups, which also determi high melting and low boiling points. Cyclic compounds ha greater viscosity than the corresponding aliphatic compounds, b in this case the introduction of a methyl group diminishes viscosit this is also the case with polymethylenes, the viscosities of whi are considerably greater than those of the corresponding aroma substances. H. J. E.

**Thermal Evolution of Gases Absorbed by Charcoals a Carbonised Lignites.** STUART McLEAN (*Trans. Roy. S Canada*, 1921, **15**, iii, 73—84).—An investigation of the he developed when air, oxygen, nitrogen, or carbon dioxide is absorb by wood or cocoanut charcoal, or lignite carbonised at vario temperatures between 350° and 550°. Oxygen develops t greatest amount of heat per unit volume of gas adsorbed. Duri the adsorption, both carbon dioxide and carbon monoxide a formed. The greatest evolution of heat per unit mass of adsorbe occurs with carbon dioxide. The thermal effect for air is mu smaller than for oxygen, and less carbon dioxide and carb monoxide are produced. In the case of oxygen adsorption, t amount of gas adsorbed diminishes until a constant value is attain on repeating the experiment. The same holds for the heat develop per unit mass of adsorbent. The heat developed by the adsorpti of carbon dioxide is not accounted for by the latent heat of evapo ation. The coarse kinds of charcoal adsorb more oxygen a form carbon dioxide more readily than other kinds. J. S. G. T.

**Influence of the Hydrogen-ion Concentration on the Pe meability of Dead Membranes, on Adsorption by Prote Sols, and on the Metabolism of Cells and Tissues.** ALBRECI BETHE (*Biochem. Z.*, 1922, **127**, 18—33).—The diffusion of ac dyes through parchment is accelerated in acid solution and depress in alkaline solution, whilst the reverse is true for basic dyes. the dyes are allowed to diffuse into a protein solution, for instanc milk, gelatin, or serum, there is preferential distribution of tl

dye in the protein solution if the acid dye is dissolved in acid solution and the basic dye in alkaline solution. The process can then be reversed by addition of alkali or acid. The analogy is extended to vital staining, where the hydrogen-ion concentration is assumed to play an essential rôle. H. K.

**Substantive Cotton Dyeing.** RUDOLF AUERBACH (*Kolloid Z.*, 1922, **30**, 166—168).—The influence of various salts on the dyeing of cotton by substantive dyes was investigated. In each case an optimum concentration of the salt was found, and this was almost inversely proportional to its precipitating power on the colloid systems. The amount of dye taken up by the threads also decreases with increasing precipitating power of the salt. The strong mineral acids do not follow the same rule, no optimum concentration being found. W. T.

**Pressure of Oxygen in Equilibrium with Silver Oxide.** FREDERICK G. KEYES and H. HARA (*J. Amer. Chem. Soc.*, 1922, **44**, 479—485).—The equilibrium pressure of oxygen over silver and silver oxide has been measured up to about 800°; the present results confirm and extend the previously published results of Lewis (*Z. physikal. Chem.*, 1906, **55**, 449). The following equation, ordinarily derived by the use of the perfect gas law and by assuming the heat constant, is found empirically to represent the data exactly: $\log p = -2859/T + 6{\cdot}2853$, where the pressure is in atmospheres, and the temperature in degrees absolute. The Nernst heat theorem as given by Pollitzer to fit the data of Lewis entirely fails to represent the present data. Neglecting only the difference in the coefficient of expansion between silver and silver oxide, the following equation is derived from the Clausius equation for the external heat of the reaction, in calories per molecule of oxygen, $Q = 6582(v - 20{\cdot}7)p/T$, where $v$ calculated from the equation of state of oxygen is given in c.c./mol. The value for the internal heat at 25°, calculated with the aid of Kopp's rule, is 12642 cal., in agreement with the mean of the measurements and computations (12640) considered by Lewis. The internal heats, although they pass through a minimum at about 400—500°, increase again with rising temperature. The analogy between this chemical reaction and a simple evaporation, therefore, breaks down, since no sign is shown of a critical point, with the heat equal to zero, although $\Delta v$ appears to be diminishing progressively. J. F. S.

**A Simple Dialyser.** A. GUTBIER and A. MAYER (*Z. anorg. Chem.*, 1922, **121**, 215—216).—A simple and efficient dialyser can be constructed as follows. A polished ring of wood, bone, or horn is grooved on the outer side, a piece of parchment paper is well soaked in distilled water and then folded over a test-tube or beaker (according to the size of dialyser required) to form a kind of bag, the glass vessel is then removed and the parchment bag tied around the ring. If necessary (for sensitive systems), in place of the ring a disk of the same material with a groove along its edge and a hole in the plate to fill and empty the bag can be used. W. T.

**Temperature Dependence of the Solubility, the Activity, and Osmotic Coefficients of Salts.** J. N. BRÖNSTED (*Z. physikal. Chem.*, 1922, **100**, 139—150).—Formulæ are developed to represent the dependence of the activity and osmotic coefficients on the temperature. These have the form $\delta \log_e f/\delta T = \alpha c/RT^2$ and $\delta\phi/\delta T = \alpha c/2RT^2$, in which $f$ is the activity coefficient and $\phi$ the osmotic coefficient, $c$ the concentration, and $\alpha = \delta U_1/\delta c$. In the case of potassium chloride in 0·1*N*-potassium chloride the value $\delta \log_e f/\delta T$ is calculated to 0·000092 and $\delta\phi/\delta T = 0{\cdot}000046$. Further formulæ are developed for the dependence on temperature of the solubility of sparingly soluble salts in pure water and in salt solutions. These formulæ have been verified by means of solubility determinations of β-cobalt croceonitrate in water, *N*/10-sodium nitrate, and potassium nitrate at various temperatures. J. F. S.

**Physical Chemistry of Lipoids. Diffusion of Methylene-blue through Organic Solvents.** S. LOEWE (*Biochem. Z.*, 1922, **127**, 231—240; cf. A., 1912, ii, 741, 742).—The author has examined qualitatively the distribution and diffusion of methylene-blue from a gelatin gel in one limb of an inverted **Y**-shaped apparatus through a supernatant organic solvent (carbon tetrachloride, benzene, toluene, ether), containing in solution one of a great variety of substances belonging to the groups of plant resins, wool-fat and its products, and various lipoids, into a gelatin gel in the other limb. With a few exceptions, the amount of methylene-blue taken up from the gelatin gel by the organic solvent and its dissolved substance and by the pure gelatin gel is small. H. K.

**Electrical Charges of Colloidal Particles and Anomalous Osmosis.** JACQUES LOEB (*J. Gen. Physiol.*, 1922, **4**, 463—486).—In a system consisting of water and salt solution separated by a collodion–gelatin membrane, the whole being on the acid side of the isoelectric point of the membrane, the transport curve of water to salt solution shows a rise up to a concentration of the salt of *M*/32, then a fall up to a concentration of *M*/4, and subsequently a continuous rise. The preliminary rise is the greater the greater the valency of the kation. On the alkaline side of the isoelectric point, curves of a similar nature are obtained, but in this case it is the valency of the anion which influences the preliminary rise.

The fluctuations in those curves ("anomalous osmosis") are explained as due to the effect of the salts on the potential difference across the membrane and on the potential difference between the solution in the pores of the membrane and the membrane itself.

Both these effects should disappear when the whole system is at the isoelectric point of the membrane; and it is, in fact, found, under these conditions, that solutions of salts composed of uni- and bi-valent ions behave like sucrose solutions. Salts containing ter- or quadri-valent kations or quadrivalent anions still behave anomalously, probably owing to the fact that the isoelectric gelatin forms loose compounds with the multivalent ions, thus setting up a potential difference between itself and the solution. C. R. H.

**An Optical Method for the Determination of the Reciprocal Solubility of Slightly Miscible Liquids.** C. CHÉNEVEAU (*Compt. rend.*, 1922, **174**, 815—817).—The process employed consists in using the method of autocollimation, whilst making it differential. The refractive indices of the liquid considered as the solvent and of the solution are measured in a specially constructed prism divided into two cells. A formula is given by means of which, from the readings taken, it is possible to calculate the solubility of the one liquid in the other. The results obtained are in very close agreement with those obtained by gravimetric methods.

W. G.

**Application of the Electron Theory of Chemistry to Solids.** (SIR) J. J. THOMSON (*Phil. Mag.*, 1922, [vi], **43**, 721—757; cf. A., 1921, ii, 252).—The part played by electrons in determining the structure of solids is considered. Each kind of atom is associated with a definite number of electrons with which it holds other atoms in chemical combination. The simplest case is that of a chemical element. In the crystalline state each unit cell will contain one atom and a definite number of electrons; one for a univalent atom, two for a bivalent atom, and so on. The arrangement of the electrons in the unit cell determines the shape of the cell and the crystalline structure. Possible unit cells are limited to (1) Parallelepipeda; (2) Hexagonal prisms; (3) Rhombic Dodecahedra; (4) Cubo-octahedra.

The univalent element gives the simplest type of cell. The atom is situated at the centre of a parallelepipedon (or cube) with an electron at each corner and each electron held in common by the atoms in eight such parallelepipeda. For a bivalent element the electrons may be arranged at the corners of an hexagonal prism or in cubes with additional electrons at the centres of one set of parallel faces. The cells of tervalent elements may be hexagonal prisms with an electron at the centre of each end, cubes with electrons at the centres of two sets of parallel faces, or as rhombic dodecahedra. Similarly, the four electrons of quadrivalent elements may be arranged as in the face-centred cube or as in the hexagonal prism with two electrons along the axis at equal distances from the centre, and so on.

The symmetries represented by the triclinic, monoclinic, rhombic, and tetragonal systems in crystallography can be obtained if an assemblage of regular cells be strained homogeneously in any way without fracture. The cells would still maintain an atom in each cell and the original number of electrons.

Making the assumptions with regard to the forces between the atoms and electrons given in the previous paper, the stability of the above electronic arrangements and their effect on some physical properties is discussed. The values for the bulk modulus, the critical frequency, and the dielectric constant calculated for elements of different valencies, agree closely with those found by experiment. Expressions are given for the potential energy per unit volume of solid, the compressibility, the latent heat of fusion, etc., for a

number of types of unit cells. It is shown that the potent energy of an atom on the surface will be greater than that in t interior of the crystal and this excess will be proportional to t surface tension.

The constitution of salts may be inferred from their physic properties. From the magnitude of the compressibility of potassiu chloride and sodium chloride it is deduced that the chlorine a sodium or potassium atoms are present as singly positively charg units with one electron per unit cell. The other six electrons a arranged as a regular octahedron about the chlorine atom at a di tance considerably smaller than the length of the cube. The numb of unit cells occupied by a chemical molecule and the presence chemical groups (for example, CN or $NH_4$) in crystals can al be indicated by compressibility measurements. It is shown th Richard's value for the compressibility of the diamond can l explained on the assumption that the carbon atoms are arrang in groups in the crystal. The stability of chains of carbon ator is discussed. A long chain of carbon atoms is unstable. A stab arrangement for chains of $CH_2$ is possible if this group be regard as equivalent to an atom of a bivalent element with two dispo able electrons. W. E. G.

**Effect of Electrolytes on the Constitution of Soap Solution as Deduced from Electromotive Force.** CYRIL SEBASTIA SALMON (T., 1922, **121**, 711—715).

**Hysteresis Phenomena and Coagulation of Sols wi Ultramicrons of Rod-like Structure, in particular Vanadiu Pentoxide compared with Fibrin Sols.** G. WIEGNER, MAGASANIK, and H. GESSNER (*Kolloid Z.*, 1922, **30**, 145—165).- Vanadium pentoxide sols contain ultramicrons of elongated ro like structures similar to fibrin sols; in course of time these ultr microns grow, this being accelerated by an increase in concentratic of the sol. The tendency to coagulate is much increased aft this growth, and can be brought about by filter-paper, boles, carbo silk threads, and silicic acid and gelatin gels. This gelatinisatic is favoured or perhaps conditioned by vanadyl salts formed l the reduction of the vanadium pentoxide. The serum obtain from the gel coagulates more sol; this is accounted for by its hi content of vanadyl salts. Salts (contained in filter-paper) favo the reduction to vanadyl salts and therefore accelerate the coag lation. Vanadic acid stabilises the sol. Dilution of sol and co sequently decrease of concentration of the active vanadie ac ions brings about gelatinisation. These results show a clo analogy to fibrin sols. Quantitative investigations are now beir carried out. W. T.

**The Protective and Flocculating Action of Hydrophil Colloids and Hydrophobic Sols.** H. FREUNDLICH and I LOENING (*Festschrift Kaiser Wilhelm Ges. Förderung Wiss. Zeh jahrigen Jubiläum,* 1921, 82—89).—It was found by Brossa an Freundlich (A., 1915, ii, 241) that the flocculating value of electr

lytes for ferric oxide sol decreased with increase in the percentage of albumin present. In addition Gann (A., 1917, ii, 21) found that egg-white had a coagulating action on acidic gold sol in the absence of electrolytes. An attempt is made to correlate these facts. By experiments with both gold and silver sols it was shown that the sensitisation of a hydrophobic sol by a hydrophilic colloid is merely a coagulation which is too slight to become immediately observable. It can be detected only by the fact that when the sol is thus sensitised, smaller amounts of electrolytes are required for flocculation. Measurements of the flocculation value of electrolytes showed that with increasing gelatin content the value diminished to a low figure. In this way the sensitisation of the ferric oxide sol by albumin is not essentially a different phenomenon from the coagulation of gold sol by egg-white. The transition from coagulating to protective action observed by Gann is a general phenomenon. It probably depends on the fact that the oppositely charged hydrophilic sol in low concentration coagulates the particles of hydrophobic sol, whereas in higher concentration the former actually envelops and thus protects them. The properties of the hydrophobic sol are thus completely masked. Silver sol protected by gelatin has the same charge as pure silver sol and is therefore not reversed in charge by addition of gelatin. The action in this case is considered due to the amphoteric nature of the protective hydrophilic colloid. CHEMICAL ABSTRACTS.

**Capillary-electric Phenomena in Lyophile Sols.** H. R. KRUYT and H. G. DE JONG (*Z. physikal. Chem.*, 1922, **100**, 250—265).—The influence of the electrolytes potassium chloride, barium chloride, potassium sulphate, potassium thiocyanate, potassium ferricyanide, sodium chloride, lithium chloride, strontium chloride, magnesium sulphate, cadmium sulphate, and lanthanum nitrate on the viscosity of agar sols of various concentrations has been measured at 50°. It is shown that above the temperature at which gelatinisation occurs (40°) agar sols follow the Poiseuille law exactly. Agar sols exhibit the quasi-viscous effect noted by Smoluchowski, and the particles are discharged by kations at concentrations corresponding with the valency of the added kation. The electrical behaviour of the agar sol is very similar to that of a suspensoid, and the electrical charge has a capillary-electric character. An emulsoid sol possesses two stabilising factors: the electric charge and the hydration, both of which must be removed before a coagulation can be effected. If the charge only is removed, a lyophile sol remains, but if the hydration is removed a suspensoid remains. Salting-out is a combined discharge and dehydration. Albuminous substances do not form ion-disperse solutions, but colloid disperse sols. The amino-acidic character exhibits itself only in the molecules which form the boundary layer of the particles and in those which form the double layer. J. F. S.

**Convertibility of Chemical Energy and the Conception of Affinity.** R. PLANK (*Z. physikal. Chem.*, 1922, **100**, 372—392).—A mathematical paper in which the maximum work of reversible

reactions is considered and from the consideration it is shown that the conception of affinity at present adopted is unsatisfactory. Suggestions are made for changing the present conception.

J. F. S.

**The Le Chatelier-Braun Principle.** Carl Benedicks (*Z. physikal. Chem.*, 1922, **100**, 42—51).—A discussion of the Le Chatelier-Braun theorem as formulated by Chwolson (*Lehrb. d. Physik*, 1905, Braunschweig). A number of cases are brought forward, chiefly metallographic, for which the theorem does not hold, and it is shown that the theorem is not generally applicable. It is always true for a system in equilibrium, and is to be regarded as a general criterion of stable equilibria, for only when the theorem holds can there be a stable equilibrium. At extremely high temperatures and pressures, the theorem holds more often.

J. F. S.

**An Explanation of Liesegang's Rings.** S. C. Bradford (*Science*, 1921, **54**, 463—464; cf. A., 1916, ii, 474; 1917, ii, 366; 1920, ii, 235, 593).—Objection is raised to the views of McGuigan (*ibid.*, 1921, **54**, 78), and particularly to the statement that the chromate of itself is unable to diffuse in the gelatin. Further, bands of lead chromate can be obtained in gelatin under suitably chosen conditions. It is maintained that the attractive force described by McGuigan is that of adsorption. A. A. E.

**Influence of Intensive Drying on Internal Change.** A. Smits (*Z. physikal. Chem.*, 1922, **100**, 477—478).—The author directs attention to the experiments of Baker (T., 1912, **51**, 2339) on the intensive drying of nitrous anhydride and nitrogen tetroxide. He points out that the large change in boiling point brought about in these substances by excessive drying probably indicates that the internal change has been stopped and that fractional distillation of such an extremely dry unary system will probably result in the separation of the pseudo-components [cf. also Baker, T., 1922, **121**, 568]. J. F. S.

**Change of Properties of Substances on Drying.** Herbert Brereton Baker (T., 1922, **121**, 568—574).

**The Dushman Equation for the Velocity of a Unimolecular Reaction.** W. E. Garner (*Nature*, 1921, **108**, 211).—It is suggested that the term $\nu$ in Dushman's equation (A., 1921, ii, 315) $\kappa = \nu e^{(-Nh\nu)/(RT)}$ is a frequency characteristic of some degree of freedom in the decomposing molecule, and is not related to the frequencies of the activating radiation. The "period of existence" of the molecule (the time corresponding with one molecular vibration) will then be $1/\nu$. It is argued, with the support of Tolman's data (A., 1921, ii, 248), that the exact agreement obtained by Dushman for observed and calculated values of $\kappa$ in the case of phosphine is accidental. A. A. E.

**Ignition Point of Detonating Gas [Hydrogen and Oxygen].** [Al]exander Mitscherlich (*Z. anorg. Chem.*, 1921, **121**, 53—66).—[The] ignition temperature of detonating gas has been determined for

ı variety of conditions in porcelain and glass tubes. The conditions which were varied, included the rate of flow of the gas, the diameter of the tube, the pressure and the dilution of the gas. It is shown that the ignition temperature of detonating gas at 150 mm. is highly lependent *on the rate of flow in the sense that it increases with lecreasing* velocity, but beyond a given velocity further increase has out a slight influence on the temperature of ignition. The following values illustrate this fact, $v=280$, $t=592°$; $v=187$, $t=592°$; $v=130$, $t=593°$; $v=93$, $t=594°$; $v=37$, $t=601°$, where $v$ is the number of c.c. passing a cross-section of 1 sq. cm. per minute. When the value of $v$ is kept constant, it is shown that the ignition temperature *increases with increasing* pressure, *thus*, $p=150$ *mm.*, $=592°$; $p=200$, $t=607{\cdot}5°$; $p=250$, $t=622°$; $p=300$, $t=630{\cdot}5°$; $p=400$, $t=644°$; $p=500$, $t=651{\cdot}5°$; $p=600$, $t=659{\cdot}5°$; $p=650$, $=663{\cdot}0°$. The diameter of the porcelain or glass tube is without nfluence on the explosion temperature for the diameters 3·6, 5·5, )·5, and 11 mm., but this is not true for narrow tubes; thus with ubes less than 0·5 mm. diameter no definite ignition temperature could be observed. J. F. S.

**Chemical Kinetics of Perchloric Acid and its Salts.** G. Bredig and J. Michel (*Z. physikal. Chem.*, 1922, **100**, 124—138).—The velocity of reaction in the reduction of aqueous perchloric acid by tervalent titanium, tervalent molybdenum, and bivalent chromium salts in hydrochloric acid and sulphuric acid solutions has been measured for various concentrations at 40°. In the case of titanium, which is most completely examined, the velocity is proportional to the first power of the concentration of the tervalent titanium, the perchloric acid, or the perchlorate. The concentration of sulphuric acid or hydrochloric acid has only very slight influence on the velocity in dilute solutions of the reactants. The influence of the acids increases from a definite acid concentration (4·45$N$-sulphuric acid, 4·69$N$-hydrochloric acid) linearly with the increasing concentration of the acids. The form of the kinetic equation is of the first order and of much lower order than is demanded by the equation representing the reaction, namely, $4Ti_2(SO_4)_3+4H_2SO_4+HClO_4=8Ti(SO_4)_2+4H_2O+HCl$. As in most similar cases, an intermediate reaction of a lower order must be assumed, the nature of which has not been ascertained. The reaction velocity of the titanium reaction increases three times for an increase in temperature of 10°. In the present experiments, the times required for an equal amount of reduction of perchloric acid in the presence of the same excess of sulphuric and hydrochloric acids at the same temperature are in the ratio : $Ti^{III}$ : $Mo^{III}$ (olive-green) : $Cr^{II}$ : $Mo^{III}$ (orange)$=1:18:1300:40000$. J. F. S.

**Kinetic Study of Alkaline Solutions of Iodine.** O. Liévin (*Compt. rend.*, 1922, **174**, 868—870).—In alkaline medium iodine is converted into iodate by processes which differ according to the degree of alkalinity. The alkali, the concentration, and the iodide formed all influence the reaction. As the amount of alkali hydroxide used for a given weight of iodine increases the free iodine

decomposes much more rapidly and occupies a position between the allyl and phenyl derivatives. The introduction of another chlorine atom reduces the velocity considerably; that is, the more symmetrical compound is the more stable. The dichloro-derivative decomposes more rapidly than its dibromo-analogue. The values of $K$ at 100° are phenylmalonic acid 0·1970, chloromalonic acid 0·1855, allylmalonic acid 0·1321, hydroxymalonic acid 0·0820, malonic acid 0·0755, methylmalonic acid 0·0598, dichloromalonic acid 0·0585, dibromomalonic acid 0·0224. W. T.

**Slow Hydrolysis of Salts.** A. Tian (*J. Chim. physique*, 1921, **19**, 190—216; cf. A., 1921, ii, 439).—The author discusses the hypothesis put forward by Wagner (A., 1913, ii, 200, 765) to explain the slow hydrolysis of salts and finds it at variance with facts, and puts forward a new hypothesis, which has the following form. The slow hydrolysis of salts is always preceded by a normal hydrolysis, limited by the reverse reaction which always occurs between ions and is extremely rapid. As soon as the solubility product of one of the substances (acid or base) produced by the hydrolysis has heen reached, a new phase appcars and at the same time a new cause of retrogradation of the hydrolysis. This supplementary retrogradation is due to a reaction between the two phases (colloid and aqueons solution) present; it is realised with a velocity which increases with the surface of contact. This cause of retrogradation is very great at first, when the colloidal particles are very small, but as a consequence of their union the surface of the particles decreases and with it the speed of the supplementary retrogradation, and from this point the hydrolysis increases. The progression of the hydrolysis is therefore as slow as the evolution of the colloid. This hypothesis has been tested by means of conductivity measurements on solutions of ferric chloride in the presence of silica gels and gelose, and found to be in keeping with the experimental data.

J. F. S.

**Catalysis. XIII. Temperature Coefficient of Catalysed and Non-catalysed Reactions.** R. M. Purkayostha and N. R. Dhar (*Z. anorg. Chem.*, 1922, **121**, 156—166).—The reaction $H_2C_2O_4+KMnO_4+MnSO_4+H_2SO_4$ has a temperature coefficient 2·96 between 10° and 20°, almost the same value as that found by Dhar for a similar reaction with chromic acid as the oxidising agent (T., 1917, **111**, 727). The reaction with permanganate is unimolecular with respect to the oxidising agent; in the case of chromic acid reaction the rate was found to be independent of the concentration of the oxidising agent. The reaction between mercuric chloride and phosphorous acid was found to be bimolecular for phosphorous acid and semimolecular for mercuric chloride. The temperature coefficient is 3·4 at 30—40° and 3·26 at 40—50°. The photochemical reactions $Na_2SO_3+O=Na_2SO_4$ and $NaClO=NaCl+O$ are discussed and are regarded as semimolecular reactions. All the reactions with a high temperature coefficient were found to be sensitive to light rays. W. T.

**Peculiar Catalytic Action in Chemical Synthesis by Glow Discharge.** FRITZ PANETH (*Z. physikal. Chem.*, 1922, **100**, 367—371).—When a glow discharge is allowed to pass through a tube containing tin electrodes and a low pressure of hydrogen, there is no combination between the hydrogen and the tin, but if the hydrogen contains a small amount of methane, tin tetrahydride is the product. The action is explained by the assumption that the excited hydrogen atom contains a higher quantic electron, and when this comes in contact with an atom of tin, vapour combination occurs. The present action is discussed in connexion with the formation of active nitrogen and triatomic hydrogen.

J. F. S.

**Reactions on Metallic Surfaces.** OTTO RUFF (*Z. physikal. Chem.*, 1922, **100**, 419—424).—It is shown that metallic calcium when alloyed with more electro-positive metals such as strontium, barium, sodium, or potassium, or with calcium nitride, combines more readily with nitrogen than pure calcium. From this observation it is concluded that the heteropolar nature of a metallic surface favours the combination with a homopolar gas, and from this it is assumed that it acquires influence charges from the surface valencies of the metal which determine its position and behaviour towards the surface. J. F. S.

**The Structure of the Atom and the Physical and Chemical Properties of the Elements.** NIELS BOHR (*Z. Physik*, 1922, **9**, 1—67).—An address delivered before the Physical and Chemical Societies of Copenhagen. A résumé is given of the recent work on the series spectra of the elements (cf. A., 1921, ii, 137) and their dependence on the orbit of the electrons within the atom. On the basis of his previous theories, the author develops an interpretation of the periodic table of the elements. In order to arrive at the relative stability of the electronic configurations in the atoms of the elements, the process of formation of an atom from the positive nucleus is followed step by step. Thus an element with an atomic number $N$ is built up by the attachment of $N$ successive electrons, each electron giving rise to a spectrum. The actual increase in charge of the nucleus, which occurs throughout the process, is taken into account. For the first two elements, hydrogen and helium, the knowledge of the spectra produced during the combining process is fairly exhaustive. For the remaining elements, the arc and spark spectra may be represented with good approximation by formulæ of the Rydberg type, $\nu=K/(n''+\alpha_{k''})^2-K/(n'+\alpha_{k'})^2$.

The orbit of the first electron is circular and the final stationary condition is attained when $n$ and $k=1$. The combination of the second electron, as the spectrum of helium shows, takes place in two different ways. In the normal condition, the second electron follows the same type of path as the first, but in a different plane and in the metastable condition it moves in a $2_1$ orbit ($n=2$ and $k=1$). The third electron, as in the lithium atom, is more loosely bound than the first two electrons and describes an eccentric orbit

$2_1$. For a small part of its path it approaches the nucleus to within a distance comparable with that of the innermost electrons. The fourth, fifth, and sixth electrons follow similar orbits. In the carbon atom, the configuration of the paths of the four loosely bound electrons possesses a tetrahedral symmetry. The seventh electron, as in the nitrogen atom, and the eighth, ninth, and tenth electrons follow circular paths of the type $2_2$, lying within the region of the type $2_1$ and being tightly bound. For neon, there will be two electrons with a path $1_1$, four electrons with elliptical paths $2_1$, and four electrons with a circular path $2_2$. The paths of the electrons of this atom will possess a high degree of symmetry. In a similar manner, the stability of the electronic configurations of the elements with higher atomic numbers is considered. Particular attention is directed to sodium, where it is shown that the first terms of the $P$ and $S$ series spectra correspond with electronic orbits $3_1$ and $3_2$, so that the last bound electron is less tightly held than the last electron in the lithium atom. With tbe beginning of the fourth period orbits of the type $4_1$ appear, but these are comparatively unstable, the outer electron of potassium being very loosely held—being only twice as fast as the corresponding $3_3$ orbit. In the case of scandium and the elements with higher atomic numbers, the $3_3$ orbits become more stable, and unsymmetrical electronic arrangements are produced which are accompanied by the appearance of colour, of paramagnetism, variable valency, and an increase in the complexity of the spectra. Throughout the first long period these irregularities occur, but when there are six each of electrons in the $3_1$, $3_2$, and $3_3$ orbits the electronic configuration again becomes symmetrical. Thus the spectra of copper becomes less complex than that of iron, and at the end of the period is found the element krypton with a very symmetrical electronic arrangement. Colour is explained as due to the transference of an electron from one orbit to another, and occurs only with an unsymmetrical arrangement of the inner electrons. In the last period of the table electrons with orbits of the type $7_1$ will be present. The Röntgen spectra also point to the same stability relationships as were found with the series spectra.

W. E. G.

**Ionisation Potential and the Size of the Atom.** A. S. Eve Trans. *Roy. Soc. Canada,* 1921, **15**, iii, 37—40).—The author tabulates the values of the respective ionisation potentials, the atomic diameters as determined by Bragg (A., 1920, ii, 537), and the cube roots of the atomic volumes, so far as these constants are all known for the elements of groups 1—7 and for the inert gases. In the first group, the products of the ionisation potential by either the atomic diameter or the cuhe root of the atomic volume are approximately constant and fairly concordant, the respective mean values being 18·3 and 15·5. It is concluded that the work done in removing an exterior electron is inversely proportional to the atomic radius. The same holds for the elements Mg, Ca, Sr, and Ba of group II, whilst the values for Zn, Cd, and Hg differ

considerably from the mean values for these four. This difference is possibly related to the fact that whilst the former have only a *single ring* of external electrons, the latter, according to Urbach, have a double ring of electrons in the outer zone. In the case of neon and argon, the diameters as deduced by Bragg afford values of the products in far better agreement with theory than those found by using the cube roots of the respective atomic volumes.

J. S. G. T.

**The Atomic Weight of *iso*Helium.** MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 145—146).—A theoretical paper in which the author applies his theory of the nucleus (this vol., ii, 208) to calculate the atomic weight of Rutherford's *iso*-helium. The assumption is made that oxygen is composed of one α-particle, four *iso*helium nuclei, and two electrons, nitrogen of one α-particle, three *iso*helium nuclei, one positively charged hydrogen atom, and two β-particles, and carbon of four *iso*helium nuclei and two β-particles. The maximum change in mass which can occur during the collision of an α-particle with atoms of oxygen, nitrogen, or carbon is taken as 0·009 unit, and from the known atomic weights of oxygen, nitrogen, carbon, helium, and hydrogen it is found that the atomic weight of *iso*helium is 3·00113±0·006.

W. E. G.

**The Genesis of the Elements.** MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 133—136).—A theoretical paper which deals with the structure of the atomic nucleus. The author proposes a modification of the Meitner nuclear model which embraces all the elements and not merely the radio-elements. Taking into account the recent work of Rutherford and Aston, he is able to give definite nuclear formulæ to the lighter elements, for example, nitrogen$=\alpha+3\alpha_1+H^++2\beta$, oxygen$=\alpha+4\alpha_1+2\beta$ ($\alpha=$Helium nucleus, $\alpha_1=$*iso*helium nucleus, $H^+=$hydrogen nucleus and $\beta=$ nuclear electrons). By making certain assumptions as to the existence of isotopes, the genetic relationship of the lighter elements is given, for example,

$$Ca_{40}\xrightarrow{\alpha}Ar_{36}\xrightarrow{\alpha}S_{32}\xrightarrow{\alpha}Si_{28}\xrightarrow{\alpha}Mg_{24}\xrightarrow{\alpha}Ne_{20}\xrightarrow{\alpha}O_{16}\xrightarrow{\alpha}C_{12}\xrightarrow{\alpha_1}Be_9\xrightarrow{\beta}B_9\xrightarrow{\alpha_1}Li_6.$$

W. T.

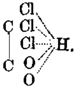
**Suggestions for the Construction of a Periodic Table on a Wider Basis.** D. BALAREFF (*Z. anorg. Chem.*, 1921, **121**, 22—24).—A method of arrangement of the elements, which takes account of the various valency states of the elements, is described. The method consists in taking nine equal rectangular sheets of glass; these are placed parallel to one another; on the first sheet all elements of zero valency are marked in the positions they would occupy in the Mendeléev system, and on the second sheet all elements which exhibit univalency are marked, and so on. Hence each sheet of glass has those elements marked on it which exhibit a given valency. On bringing the sheets close together, the Mendeléev system is obtained, but at the same time relationships depending on the valency are brought out and emphasised.

J. F. S.

**Twenty-eighth Annual Report of the Committee on Atomic Weights. Determinations Published during 1921.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 427—437).—The report of the Atomic Weight Committee is discussed, and much of the numerical data concerned with recent determinations of the atomic weight of oxygen, fluorine, chlorine, nickel, zinc, germanium, cadmium, antimony, lanthanum, and bismuth is reproduced. J. F. S.

**An Electrical Doublet Theory of the Nature of the Molecular Forces of Chemical and Physical Interaction.** R. D. KLEEMAN (*Physical Rev.*, 1921, **18**, 303—312; cf. A., 1910, ii, 492).—It has already been shown that the attraction between two atoms is proportional to the product of the square roots of their atomic weights; the suggestion is now made that a neutral atom with a positive nucleus surrounded by electrons is an electrical doublet. Since the force between two such doublets would on the average be an attraction proportional to the product of the moments of the two doublets, it follows that the electrical moment of an atom is proportional to the square root of its atomic weight. A. A. E.

**Nature of the Ionogen Linking.** HUGO KAUFFMANN (*Z. physikal. Chem.*, 1922, **100**, 238—249).—It is shown that the introduction of methoxyl groups into the ortho- and para-position of triphenyl carbinol, fuchsines, and similar substances increases the basic character of these substances, whilst in the meta-position the basic character is unchanged. It is shown that the basicity is not centralised in one carbon atom, but distributed over all the ortho- and para-positions and that every methoxyl group introduced in those positions has an active share of the total basicity of the compound. In salts with a radicle as kation, the basic character is not centralised, but is spread over the whole kation, and consequently the positive charge of the kation is not situated on a single atom but is spread over the whole ion. The valency of an anion in union with such an ion is therefore a divided valency which acts in parts between the anion and the positions on the kation where the positive charge is located. Hence the ionogen linking is a divided linking. In the case of acetic acid it is represented as $CH_3{\cdot}C_{O}^{O}{>}H$ and in trichloroacetic acid as in



the annexed formula. The author then discusses homo- and hetero-polar linkings, and shows that these are only limiting cases and that most linkings are intermediate between these. From the discussion, the following results are drawn. The valency has its seat in the atomic nucleus. Valency is measured by the number of lines of electric force which lead from the nucleus of an atom to the connecting electrons. To bring this statement into line with the usual chemical valency numbers, it is necessary to divide the abovementioned number by $4\pi e$, where $e$ is the absolute value of the charge of an electron. A result of this statement is that all valencies

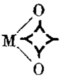
are positive; negative valencies are impossible and that which has hitherto been termed negative valency is the other end of the line of force from the electron. The characteristics of the homo- and hetero-polar linkings are illustrated by means of the electric moment. If $M_A$ represents the electric moment of the valency of an atom $A$, $M_B$ that of an atom $B$, and $M_{AB}$ that of the linking $A$–$B$, then $M_{AB}=M_A-M_B$. If the atom nucleus of $A$ is similar to that of $B$, then $M_{AB}$ is zero. It follows that the electric moment of a pure homopolar valency is always zero. When $M_{AB}$ is equal to $M_A$, the linking is heteropolar and the electric moment is the greater the more pronouncedly heteropolar is the linking. J. F. S.

**Double and Triple Bonds, and Electron Structures in Unsaturated Molecules.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 438—451).—A theoretical paper dealing with electron structure of unsaturated molecules of compounds of carbon, nitrogen, and boron. It is suggested that multiple linking involves the transfer of two electrons from the inner to the outer shell in one or both of two atomic nuclei, the group of eight being preserved about each, with two jointly held electrons constituting the hond. This hypothesis is sufficient to explain the restricted region of the periodic system in which elements characterised by multiple bond formation occur. To meet requirements imposed by the facts relating to stability, reactivity, and free rotation, the electrons of unsaturated octets are assumed to be held in equilibrium positions at greater distances from the nucleus than in the ordinary case, the transfer from the extended position to the usual one liberating energy. No attractive force between electrons is assumed, and the electron arrangement is taken as cubic, although subject to distortion. On this basis, a mechanism is provided for addition and condensation reactions. Many interesting points of view are afforded in the study of conjugation, the structure and substitution reactions of benzene, and tautomeric displacement of double bonds. Formulæ are illustrated and discussed which represent, more satisfactorily in several cases than other current hypotheses, many of the properties of chain hydrocarbons, the oxides of carbon, the carbonyl and carboxyl groups, nitrogen, oxygen, and the hydrides and oxygen-containing ions of boron.

J. F. S.

**Mesohydry. II.** GIUSEPPE ODDO (*Gazzetta*, 1922, **52**, i, 42—56).—A claim for priority (cf. A., 1907, ii, 15) principally over Kauffmann (*Ahrens Sammlung*, 1907, **11**, 1—102; 1918, **12**, 1—112), Gebhard (A., 1912, ii, 242), and Hantzsch (A., 1908, ii, 462; A., 1910, i, 200). T. H. P.

**Mesohydry. III. Relation between the Affinity of Acids and the Atomic Ratio O : H in their Functional Groups, and the Constitutional Formulæ of the Acids.** GIUSEPPE ODDO (*Gazzetta*, 1922, **52**, i, 56—79; cf. A., 1907, ii, 15, and preceding abstract).—Starting with the conception that tetragonal meso-

hydric nuclei, , are not capable of dissociation and tha they become so in solution only in so far as they undergo hydrolyti transformation into the group, O:M·OH, the author shows tha an intimate relation exists, for all acids, between the number c oxygen and hydrogen atoms existing in the functional acid grou and the force of affinity.

With the monobasic acids, there are the following five differen types, that in which $n$O : $n$H has the value 2 : 1 required b the non-ionisable mesohydric nucleus, being taken as a basis (1) $n$O : $n$H=4 : 1, acids even more energetic than HCl, such a $HClO_4$; (2) $n$O : $n$H=3 : 1, acids as energetic as HCl, such a $HClO_3$; (3) $n$O : $n$H=2 : 1, very weak acids, such as R·$CO_2$H (4) $n$O : $n$H=2 : 2 (or more), acids somewhat more energetic thai the 2 : 1-acids, such as $H_2CO_2$; (5) $n$O : $n$H=1 : 1 (or more), ver feeble acids, such as HClO.

With the dibasic acids, if the oxygen and hydrogen atoms con stituting the dibasicity are distributed between two oxidisabl atoms, the relations for each of the acid functional groups thu resulting are the same as for the monobasic acids, except for th mutual influence of the two groups, this being marked in the 1 : 2 position, slight in the 1 : 3-position, and almost zero in the 1 : 4 position. Thus, succinic acid is almost equivalent to acetic aci in this respect, and dithionic acid to nitric acid or to R·$SO_3$H If, however, the oxygen and hydrogen atoms causing the dibasicit are united to the same oxidisable atom, only two types result (1) $n$O : $n$H=4 : 2, acids of the average energy of monobasic acid of types (1) and (2), for instance, sulphuric acid; (2) $n$O : $n$H= 3 : 2, very weak acids, such as $H_2SO_3$ and (3) $n$O : $n$H=2 : 2, stil weaker acids, such as $H_2SO_2$. With tri- and poly-basic acids, th relations are the same as with dibasic acids. T. H. P.

**Space Formulæ.** FRIEDRICH RINNE (*Z. physikal. Chem.* 1922, **100**, 408—418).—A theoretical paper in which the spacia configuration of crystalline substances and the atomic diamete are considered on the bases of the Barlow and Pope hypothesis of close packing, the molecular volume, and the *X*-ray measure ments of crystal structure. J. F. S.

**Still-head for the Prevention of Spray.** FRIEDRICH L. HAHN (*Z. anal. Chem.*, 1922, **61**, 52—53).—The lower end of the delivery tube, below the cork closing the distillation flask, is blown into the form of an elongated bulb of slightly smaller diameter than that of the neck of the flask. An internal tube extends from an opening at the shoulder of the bulb to nearly the bottom of the latter, and the bulb itself is filled with pieces of broken glass The vapours from the flask pass through the tube into the bulb, and then escape through the delivery tube to the condenser. Since

the bulb is contained in the neck of the flask, reflux action is but slight and distillation is rapid. W. P. S.

**A Sodium Press for the Laboratory.** Ernst Beckmann (*Ber.*, 1922, **55**, [*B*], 766—768).—The instrument is figured and fully described in the original. The essential features are the construction of the press cap in two separable portions whereby cleaning is greatly facilitated, the arrangement of the piston in such a manner that it has only a vertical and not a rotatory motion, the provision of a powerful wheel in place of the handle usual in copying presses, and a calibration device whereby the weight of the sodium wire can be ascertained from the readings of the rotations of the wheel. H. W.

**Apparatus for Hydrogenation at Ordinary Pressures.** J. Klimont (*Chem. Zeit.*, 1922, **46**, 275).—An ordinary distillation flask of about 150 c.c. capacity has a glass tube sealed horizontally into the neck and bent at right angles inside the flask so that it passes vertically downwards, and ends in a small depression blown in the bottom of the flask, which is also provided with a rubber stopper carrying a short glass tube bent at right angles, which may be connected with a manometer, and a thermometer dipping into the liquid in the flask. The flask is filled by means of a long-stemmed funnel with a mixture of the substance to be hydrogenated and the catalyst, which is heated by means of a Bunsen burner and kept in constant agitation by a stream of hydrogen, which enters through the tube dipping into the liquid and leaves through the other side tube. H. C. R.

**A Reversible Turbidity Phenomenon.** Raphael Ed. Liesegang (*Kolloid Z.*, 1922, **30**, 165—166).—The double salts mercuric silver iodide and copper silver iodide undergo a colour change at 70° and 45°, respectively, and have found application as colour thermoscopes. A similar change at a lower temperature is produced by a mixture of 18 c.c. of 10% gelatin solution, 1 c.c. of 20% potassium ferricyanide, and 1 c.c. of nitric acid (*d* 1·148). This is completely clear, but becomes opaque on solidification and again clear on liquefaction. After hydrolysis of the gelatin, the turbidity is fainter. Nitric acid can be replaced by hydrochloric, citric, and other acids. W. T.

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## Inorganic Chemistry.

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**Triatomic Hydrogen. II.** Gerald L. Wendt and Robert S. Landauer (*J. Amer. Chem. Soc.*, 1922, **44**, 510—521; cf. A., 1920, ii, 425).—Triatomic hydrogen has now been prepared by three new methods, the Siemens glass tube ozoniser, the high frequency Tesla discharge, and the thermionic emission methods. Attempts to show its presence in hydrogen produced as nascent hydrogen from

solutions of hydrogen-ions were unsuccessful. This hydrogen i catalytically decomposed by finely divided platinum, nickel, coppe lead, antimony, and cadmium. It is unaffected by contact wit silver, mercury, tin, bismuth, molybdenum, zinc, or aluminiun Contraction in volume occurs when this hydrogen is produced b the electrical discharge at 3 mm. pressure. This is particularl marked at the temperature of liquid ammonia and solid carbo dioxide. Triatomic hydrogen is condensed to the liquid form h exposure to the temperature of liquid oxygen. The spectrum c hydrogen at the temperature of liquid oxygen shows a pro gressive intensification of the secondary line spectrum at th expense of the primary series spectrum, which is probably due t the gradual formation of the triatomic form. The present wor is held to confirm the mechanism of the formation previousl advanced, and also it shows that the new gas is probably $H_3$ an not *iso*-$H_2$, an atomic species proposed by Harkins as a constituen of heavier atoms (cf. Harkins, A., 1920, ii, 479, 745). J. F. S.

**Constitution of Haloids.** WILHELM BILTZ (*Z. physika Chem.*, 1922, **100**, 52—67).—A theoretical paper in which th author discusses the constitution of the haloids from consideration of the melting point, temperature of decomposition, and electro lytic conductivity of the molten compounds. In the case of th platinum, iridium, and vanadium compounds, it is shown tha the heat of formation of the highest chloride is much less tha that of the remaining lower chlorides; he therefore considers tha the higher chlorides are to be considered as co-ordination com plexes of the same type as the ammines. In the case of the meltin points of the chlorides, it is shown that the lower chlorides hav much lower values than the higher chlorides, and in the same wa the lower chlorides have a much smaller conductivity in the molte condition than the higher chlorides. All haloids melting betwee 960° and 450° are good conductors, those melting between 450 and 200° are partly good conductors, partly poor conductors, an some do not conduct at all, and those melting below 200°, wit the exception of the gallium compounds, do not conduct at al The lower chlorides are therefore regarded as true salts, whilst th higher compounds are regarded as complexes. A comparison o the electro-valency towards chloride with the atomic numbe indicates periodicity as shown by a curve made by plotting th two values. J. F. S.

**Significance of the Density of Hydrogen Bromide wit Reference to the Atomic Weight of Bromine.** GREGOR PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 595—601; c Guye, A., 1919, ii, 333).—A discussion on the determination o atomic weight from gas densities, particularly in the case of th atomic weight of bromine from the gas density of hydrogen bromide The pitfalls of such determinations are carefully described. It i pointed out that no method of extrapolation can be satisfactor or convincing where, as in the case of hydrogen bromide, th curacy of the numerical data diminishes as the region to b

extrapolated approaches. The conclusion cannot be avoided that whilst in the case of hydrogen bromide the gas density method of determining molecular weights may be regarded as an interesting and satisfactory corroboration of gravimetric evidence, its value ceases at that point. To use such as a criterion on which to judge the best gravimetric evidence cannot be justified on scientific grounds. On the other hand, from the point of view of the general application of Avogadro's hypothesis to gases at low pressures, the results of the very careful density determinations, published from Guye's laboratory, are particularly significant and convincing.

J. F. S.

**Adsorption of Iodine by Silver Iodide.** FRANK E. E. GERMANN and RALPH N. TRAXLER (*J. Amer. Chem. Soc.*, 1922, **44**, 460—464).—Carey Lea's experiments indicate that iodine is strongly adsorbed from solution by silver iodide (A., 1888, 1). This point has been investigated; dry thoroughly washed silver iodide precipitated from $N$-solutions of silver nitrate by potassium iodide was added to aqueous and alcoholic solutions of iodine, but there was no appreciable adsorption. In the same way, moist silver iodide precipitated from $N$- and $0{\cdot}1N$-solutions of silver nitrate gave negative results. Decolorisation of the iodine solution was obtained with unwashed silver iodide both from $N$- and $0{\cdot}1N$-solutions, using an excess of silver nitrate. The decolorisation was due to a chemical reaction between the iodine in solution and the silver nitrate occluded in the silver iodide and adsorbed on its surface. Unwashed silver iodide precipitated from dilute solutions of silver nitrate and potassium iodide decolorised the iodine solutions most easily, due to the greater adsorption of silver nitrate by the silver iodide and the larger quantity of solution held because of the increased porosity. A sherry-red solution of iodine in alcohol contains about 0·008 millimol. per c.c. From the above, it is concluded that there is no adsorption of iodine from solution by silver iodide above a maximum limit of 0·02 millimol. per gram of silver iodide. Hence if Carey Lea worked with 25 c.c. of sherry-red solution of iodine, he must have added more than 10 grams of silver iodide to obtain complete decolorisation. J. F. S.

**Vapour Pressure of Selenium Oxychloride.** VICTOR LENHER, G. B. L. SMITH, and G. G. TOWN (*J. Physical Chem.*, 1922, **26**, 156—160).—The vapour pressure of selenium oxychloride has been determined at temperatures from 84·3° to 117·2° by means of a modified Ramsay and Young apparatus and from 123·5° to 177·2° by the distillation method. The results are recorded for every degree over the whole range of temperature. The vapour pressure is expressed by the formula $\log P = 5{\cdot}8503 + 0{\cdot}000219T - 830{\cdot}9/(T - 178)$, where $P$ is the pressure in millimetres of mercury and $T$ the temperature in absolute degrees. Selenium has no influence on the vapour pressure between 90° and 120°, selenium monochloride has no influence on the vapour pressure between 91° and 135°, neither does selenium tetrachloride up to its saturation point show any effect between 89° and 130°. Selenium oxychloride,

when distilled under reduced pressures, has a light straw colour m. p. 10·8°, b. p. 177·2°/744 mm.; when distilled under atmospheric pressure, it decomposes slightly and becomes reddish-brown; this decomposition reverses to some extent on cooling. There is a small amount of dissociation between 265° and 290°, since the mean value of the molecular weight over this range of temperature is 151·4. The following minor decompositions occur at or near the boiling point under atmospheric pressure. $2SeOCl_2 \rightleftharpoons SeO_2+SeCl_4$; $2SeCl_4 \rightleftharpoons Se_2Cl_2+3Cl_2$; $2Se_2Cl_2 \rightleftharpoons SeCl_4+3Se$; and $4SeOCl_2 \rightleftharpoons Se_2Cl_2+2SeO_2+3Cl_2$. J. F. S.

**Nitrosylselenic Acid.** JULIUS MEYER and WALTER WAGNER (*Ber.*, 1922, **55**, [*B*], 690—692).—*Nitrosylselenic acid*, $NO{\cdot}O{\cdot}SeO_2{\cdot}OH$, a colourless, crystalline, snow-like mass, is obtained by the action of liquid nitrogen trioxide on ice-cold, anhydrous selenic acid, a large excess of the former being used initially and the greater part being subsequently allowed to evaporate. It has m. p. 80° (decomp.). It is somewhat unstable even at the atmospheric temperature, and is immediately decomposed by water. H. W.

**Cathodic Reduction of Elementary Nitrogen.** FR. FICHTER and RICHARD SUTER (*Helv. Chim. Acta*, 1922, **5**, 246—255).—Tschirch's view that absorption of atmospheric nitrogen by leguminous plants is due to electronic action receives support from the work of Hiedemann (A., 1921, ii, 694). Since, further, biochemical oxidation can be reproduced electrochemically by use of high potential differences (Fichter, this vol., ii, 23), the attempt has been made to reduce nitrogen to ammonia by similar means. Rayleigh's contradiction (T., 1897, **71**, 181) of Davy's original positive result can be disregarded, since he employed platinum electrodes and a high current density instead of gold electrodes and a low density. Experiments are now described in which, after making full allowance for the effects of impurities by blank experiments, on an average 0·3 mg. of ammonia per 160 amp. min. was consistently obtained from nitrogen under 200 atm. pressure by the use of platinum electrodes of large surface, freshly and thickly platinised, the electrolyte being 1% sulphuric acid (cf. Fischer and Priess, A., 1913, ii, 285; Tiede and Schleede, A., 1921, ii, 328). The cathode surface quickly loses its efficiency, and has to be renewed. Its activity cannot be restored by oxidation (Willstätter and Waldschmidt-Leitz, A., 1921, ii, 185). No definite evidence of ammonia formation could be obtained when a mercury cathode was employed. J. K.

**Formation and Decomposition of the Higher Nitrogen Oxides.** MAX BODENSTEIN, FRIEDRICH BOËS, (FRL.) LINDNER, and RAMSTETTER (*Z. physikal. Chem.*, 1922, **100**, 68—123).—The equilibria $N_2O_4 \rightleftharpoons 2NO_2$ and $2NO_2 \rightleftharpoons 2NO+O_2$ have been investigated over the temperature range 281·7 to 403·8° Abs., and 498·9° to 825·3° Abs., respectively. The velocity of the reaction $2NO+O_2=$ con has been determined at a series of temperatures. It is shown curacye equilibrium $2NO_2 \rightleftharpoons N_2O_4$ is represented by the formula

og $p^2_{NO_2}/p_{N_2O_4}$=log $k_p$=$-2692/T+1{\cdot}75$ log $T+0{\cdot}00483T-7{\cdot}144\times$ $0^{-6}T^2+3{\cdot}062$. This equation embodies the measurements of Vourtzel (A., 1920, ii, 108) between 0° and 84°, and the corrections nade by the authors on measurements of the rate of oxidation of iitric oxide. The dissociation $2NO_2 \rightleftharpoons 2NO+O_2$ is to be repreented by the equation log $p^2_{NO} \cdot p_{O_2}/p^2_{NO_2}$=log $k_p$=$-5749/5+1{\cdot}75$ og $T-0{\cdot}00050T+2{\cdot}839$. Both constants are true for values of measured in atmospheres. The experimental measurements in oth the above cases were effected by introducing suitable quantities f pure nitrogen tetroxide into a quartz flask and measuring the ressure with a quartz glass manometer at different temperatures. he older measurements on the velocity of combination of oxygen ith nitric oxide at lower temperatures (0—90°) and low pressures ere extended to higher temperatures (140—390°), at which the everse reaction is considerable. The measurements were made, s before, by observing pressure changes as indicated by a bromoaphthalene manometer. The reaction takes place, as expected, ccording to the equation $dx/dt=kC_{O_2} \cdot C^2_{NO}-k'C^2_{NO_2}$. The velocity icreases with increasing temperature, but more slowly the higher he temperature, until eventually it is practically independent of he temperature. According to the present observations, the ecomposition of nitrogen dioxide must also be measurable, and ieasurements were made at temperatures of 319—383° and the elocity shown to be given by $dx/dt=k'C_{NO_2}-kC^2_{NO} \cdot C_{O_2}$. The alue of $k'$ increases with temperature 1·5 times for an increase f 10°; $k/k'$ gave a good agreement with the value of $K$ deduced rom the measurements. The theory of gas reactions of the third rder is considered, and it is shown that simultaneous collisions etween three molecules are not too few to give true trimolecular eactions, as is stated by Trautz (A., 1916, ii, 422). In the present ork at 0°, where the greatest velocity is observed, it is shown hat one hundred thousand times as many such collisions occur s lead to reaction, and that, from the variation of the interval etween collisions of two molecules with the temperature and the robability of triple collisions, the unusual dependence of this eaction on the temperature may be deduced. J. F. S.

**Purification of Phosphoric Oxide.** George Ingle Finch nd Raymond Harold Kelsall Peto (T., 1922, **121**, 692—693).

**The Behaviour of Amorphous Carbon and Sulphur when leated: Sulphides of Carbon.** J. P. Wibaut (*Rec. trav. chim.*, 922, **41**, 153—171; cf. A., 1919, ii, 190; also Mixter, A., 1893, , 571).—The sulphur which is retained by carbon after a mixture f the two elements has been heated has now been further investiated and the author considers that it is chemically combined, lthough no definite compound has been isolated. The product probably a mixture of carbon with a sulphide of carbon which practically non-volatile at 1000°, although the quantity of ilphur retained depends on the nature of the carbon and on the xtent of its surface (cf. Langmuir, A., 1915, ii, 467). It is pointed ut that these results are analogous to those obtained by Lowry

and Hulett (A., 1920, ii, 536) and by Rhead and Wheeler (T., 1912, **101**, 831, and 1913, **103**, 461) in the case of carbon and oxygen. It is suggested that the sulphur present in coal as iron pyrites is fixed by the carbon in the process of coking. H. J. E.

**Processes in Gas Generators and Blast Furnaces.** H. von Jüptner (*Z. physikal. Chem.*, 1922, **100**, 231—237).—A theoretical paper in which relationships between carbon monoxide and carbon dioxide in gas generators and blast furnaces is discussed. It is shown that the direct reduction of iron oxide by carbon in the blast furnace is advantageous, for it involves a reduction in the amount of fuel used, but the process is slow. In the electric blast furnace, better results are obtained with porous wood charcoal than with the denser coke, and also the liquid condition of the ore accelerates the process. J. F. S.

**The State of Carbonic Acid in Aqueous Solution.** A. Thiel (*Z. anorg. Chem.*, 1922, **121**, 211—214).—A theoretical paper. Wilke (this vol., ii, 52) assumed that the increase in the strength of carbonic acid caused by the addition of neutral salts is due to the formation of orthocarbonic acid. This is shown to be incorrect. No other explanation is offered. W. T.

**Solubility of Potassium Permanganate in Solutions of Potassium Sulphate and Sodium Sulphate.** H. M. Trimble (*J. Amer. Chem. Soc.*, 1922, **44**, 451—460).—The solubility of potassium permanganate in solutions of sodium sulphate and potassium sulphate of concentrations varying between 0 and 10·75% and 0 and 21·80%, respectively, have been determined at 25°. The densities of the mixed solutions and of solutions of the single salts have also been determined for a series of concentrations. It is shown that the solubility of potassium permanganate in solutions of potassium sulphate decreases with increasing concentration of the sulphate. In solutions of sodium sulphate the solubility increases to a maximum with increasing concentration of sodium sulphate. The maximum solubility lies at about 6% of sodium sulphate, after which there is a slow decrease in solubility to a minimum in solutions which contain the maximum amount of sodium sulphate soluble in the presence of permanganate crystals. For the lower concentrations of each sulphate, potassium sulphate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulphate, whilst sodium sulphate increases its solubility in solutions of potassium sulphate to a much smaller degree. J. F. S.

**Thermal Decomposition of Potassium Permanganate.** E. Moles and M. Crespi (*Z. physikal. Chem.*, 1922, **100**, 337—345).—The thermal decomposition of potassium permanganate has been investigated at temperatures up to 542°. It is shown that pure dry potassium permanganate shows the first signs of decomposition at 200°. The pressures observed when permanganate is heated at lower temperatures than this are due to the presence of carbonates and substances containing water. The

decomposition is complete at 240°, and the oxygen pressure of the residue up to 485° corresponds with that of pure manganese dioxide. From 485° upwards the two dissociation curves diverge from one another, and this divergence indicates the formation of the complex assumed by Askenasy and Solberg (A., 1912, ii, 1167). The absorption equilibrium does not coincide with the liberation equilibrium, a behaviour which is also observed with manganese dioxide. From the dissociation values of potassium permanganate, the heat of dissociation has been calculated and the value 60,000 cal. obtained. The absence of potassium hydroxide in the residue after heating has been established from conductivity measurements, and it is therefore proved that potassium oxide is not one of the decomposition products of potassium permanganate as indicated by Rudorf (A., 1901, ii, 388) in the equation $10KMnO_4=3K_2MnO_4+7MnO_2+2K_2O+6O_2$; consequently it is assumed that manganite must be formed according to the equation $10KMnO_4=2K_2MnO_4+3K_2MnO_3+5MnO_2+6O_2$. J. F. S.

**Electrolytic Production of Sodium Perborate.** Peder Chr. Alsgaard (*J. Physical Chem.*, 1922, **26**, 137—155).—A long account of experimental work on the electrolytic preparation of sodium perborate is given (*Tidskr. kem. Farm. Terap. Kristiania*, 1916, Nos. 17, 18), which is followed by an account of the author's own experiments. It is shown that by electrolysing a solution containing 45 grams of borax, 130 grams of sodium carbonate, 45 grams of sodium hydrogen carbonate, 2 grams of potassium dichromate, and 2 grams of sodium silicate per litre at 10° between a suitably shaped copper pipe as cathode and a platinum anode by means of a current of 6 amperes at 7—8 volts a yield of 11·55 grams of sodium perborate per litre may be obtained. This corresponds with a 40% current efficiency. [Cf. *J. Soc. Chem. Ind.*, 1922, 326A.] J. F. S.

**The Preparation of Sodium Hydrogen Carbonate.** E. Toporescu (*Compt. rend.*, 1922, **174**, 870—873).—A study of the equilibrium of the four salts, sodium chloride, sodium hydrogen carbonate, ammonium chloride, and ammonium hydrogen carbonate, with their saturated solutions at 15°, together with measurements on certain mixtures of two or three of them together. From the results, a solubility diagram has been constructed by Le Chatelier's method (cf. A., 1921, ii, 248). From this diagram it is possible to calculate the amount of the different salts which will crystallise when a solution of known initial composition is progressively evaporated. W. G.

**The Manufacture of Sodium Carbonate by the Ammonia Process.** H. Le Chatelier (*Compt. rend.*, 1922, **174**, 836—841).—Using the results of Toporescu (cf. preceding abstract), diagrams are constructed by means of which it is possible to calculate the theoretical yields in the ammonia–soda process, under different conditions, and starting with mixtures of any initial composition. The theoretical maximum yield may be considerably reduced by

very slight changes in the initial composition. These results, obtained by studying the concentration of solutions initially very dilute, are applied to manufacturing conditions in which salts are added to a fixed amount of water, which is kept constant throughout the separation of the sodium hydrogen carbonate. It is possible to calculate the amount of water, on the one hand, or salt, on the other, which it may be necessary, under the manufacturing conditions, to add in order to get the maximum yield of pure sodium hydrogen carbonate. W. G.

**Density of Aqueous Solutions of Ammonium Perchlorate.** A. Mazzucchelli and S. Anselmi (*Gazzetta*, 1922, **52**, i, 147—152).—The densities of aqueous ammonium perchlorate solutions of $p\%$ concentration or $n$-normality are given by the equations, $d_{15}=0{\cdot}99913+4{\cdot}6826\,.\,10^{-3}\,.\,p+1{\cdot}425\,.\,10^{-5}\,.\,p^2+2{\cdot}10^{-7}\,.\,p^3$; $d_{25}=0{\cdot}99907+4{\cdot}7898\,.\,10^{-3}\,.\,p+1{\cdot}920\,.\,10^{-5}\,.\,p^2+1{\cdot}33\,.\,10^{-8}\,.\,p^3$, and $d_{15}=0{\cdot}99913+5{\cdot}632\,.\,10^{-2}\,.\,n-5{\cdot}24\,.\,10^{-4}\,.\,n^2-5{\cdot}2\,.\,10^{-5}\,.\,n^3$. The results show that ammonium perchlorate dissolves in water with increase of volume at 25° and with decrease of volume at 15°, and thus support de Boisbaudran's view (cf. Roozeboom, "Heterogene Gleichgewichte," II, i, 402) that no fundamental distinction can be drawn between salts dissolving with contraction and those dissolving with expansion of volume. T. H. P.

**The Decomposition of Ammonium Nitrate by Heat.** Horace Leonard Saunders (T., 1922, **121**, 698—711).

**The Ammonium Carbonate–Carbamate Equilibrium.** Rudolf Wegscheider (*Z. anorg. Chem.*, 1921, **121**, 110—112).—A theoretical paper in which the author makes an attempt to explain the divergences of the views of Faurholt (this vol., ii, 272) and the author (A., 1916, ii, 617) in connexion with the equilibrium in a solution of ammonium carbamate. It is shown that the equilibrium in such solutions cannot be regarded as definitely settled until some hypothesis is put forward which will explain the older results and those of Faurholt, or until it is shown that the results of Fenton and of Burrows and Lewis, despite their agreement, are erroneous. J. F. S.

**Purity of Atomic Weight Silver. I. Gases in Pure Silver and Iodine.** Gregory Paul Baxter and Leon Woodman Parsons (*J. Amer. Chem. Soc.*, 1922, **44**, 577—591).—The amount f gases contained in silver and iodine which has been purified for tomic weight work has been determined. It is shown that iodine ublimed in air yields small quantities of gases when resublimed a vacuum. The proportions varied from 0·0005% in the case f crude iodine to 0·00015% in the case of the purest material. These proportions are far smaller than those found by Guye and ermann (A., 1914, ii, 727). Crude silver, when converted into odide in a vacuum, was found to yield 0·006% of gas, whilst the urest material when treated in the same way yielded only 0·00063%. n this case also, the proportion of gas found in the pure metal

is only one-seventh that found by Guye and Germann. The foregoing figures are based on the assumption that the iodine and the silver are responsible for all the gas evolved, and that the gas is as heavy as air. It has been shown to be likely that a portion of the gas obtained was either liberated from the walls of the apparatus or diffused through the reaction tube. Furthermore, in the case of silver, at least, a large portion of the gas was found to be hydrogen. There is therefore good reason to believe that the real percentages are smaller than those given above. When the maximum corrections are applied, the atomic weights of silver and of elements referred to silver are affected in the most unfavourable cases by only 0·002 unit. J. F. S.

**Purity of Atomic Weight Silver. II. Solid Impurities.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 591—594; cf. preceding abstract).—Atomic weight silver when examined spectroscopically shows the presence of only calcium as impurity, and this in an amount not greater than 0·00004%. It is therefore concluded that in the present state of the most accurate chemical analysis the purity of atomic weight silver is fully adequate. J. F. S.

**The Absorption of Nitrogen by Calcium and its Alloys.** OTTO RUFF and HELLMUTH HARTMANN (*Z. anorg. Chem.*, 1922, **121**, 167—177).—Methods of preparing calcium alloys are given. The rate at which alloys rich in calcium absorb nitrogen depends on volume relationship, temperature, potential of the added metal, and the calcium nitride content of the alloy. The contraction of calcium in the formation of calcium nitride keeps the exposed surface porous, but pure calcium is almost passive towards nitrogen. Metals more strongly positive than calcium accelerate the adsorption (K, Ba), of the others, some have no effect (Mg, Pb, Sn), others retard it (As, Sb), and some inhibit it (Bi, Cu, Zn). The addition of more positive metals has a loosening effect on the valency electrons of calcium. Calcium nitride acts as a catalytic agent in all cases. With calcium alloys containing 5% of the nitride, pure argon can be obtained from atmospheric nitrogen in a few minutes even at a temperature below 320°. W. T.

**Zinc Borate.** T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1922, **59**, 265—268).—The admixture of solutions containing equivalent weights of zinc sulphate and borax causes the precipitation of a gelatinous mass, which is very difficult to filter and wash. When dry, it contains boric acid, even after prolonged washing, but zinc oxide is also present. The precipitate is soluble in boric acid solution if it is kept moist, but becomes insoluble when dried. S. I. L.

**Thallous Nitrite in certain Complex and Double Nitrites.** V. CUTTICA and A. PACIELLO (*Gazzetta*, 1922, **52**, i, 141—147).—Although thallium closely resembles in physical properties the heavy metals, thallous nitrite exhibits a chemical and physico-chemical behaviour quite different from that shown by the nitrites

of these metals. In aqueous solution, thallous nitrite, like the alkali nitrites, is highly dissociated, and the salt shows no tendency to form either complex or double nitrites. In the compounds described below, this nitrite enters with the character of the alkali nitrites.

*Cupric thallous nitrite* [*thallous cuprinitrite*], $Tl_3[Cu(NO_2)_5]$, forms opaque, black, rounded crystals, yields pale green, aqueous solutions, and is decomposed by dilute acid, with formation of a blue solution and liberation of nitrous acid. At the ordinary temperature, both the solid salt and its aqueous solutions are stable.

In order to trace the displacement of the equilibria produced in solution of cupri-nitrous complexes by variation of the relative concentrations of the components, conductivity measurements have been made on solutions containing cupric chloride and barium nitrite in different proportions. The conductivity–composition curve shows two inflexions, due to the appearance of two complexes corresponding with the ions $[Cu(NO_2)]$ and $[Cu(NO_2)_2]$.

*Thallous nickelonitrite*, $Tl_4[Ni(NO_2)_6]$, forms stable, flesh-red crystals and yields stable, green, aqueous solutions.

*Barium thallous nitrite*, $TlNO_2,2Ba(NO_2)_2$, forms golden-yellow, prismatic crystals and is stable in the air and very readily soluble in water.

*Lead thallous nitrite*, $Pb(NO_2)_2,2TlNO_2,H_2O$, forms orange-yellow crystals and in aqueous solution, especially when heated, undergoes partial hydrolysis with separation of lead hydroxide. T. H. P.

**Thallium Bismutho-, Stibio-, and Arseno-thiosulphates.** G. Canneri (*Gazzetta*, 1922, **52**, i, 37—41; cf. Carnot, A., 1877, i, 50; Hauser, A., 1903, ii, 487; Szilágyi, A., 1921, ii, 199, 207).—*Thallous bismutho-thiosulphate*, $Tl_3Bi(S_2O_3)_3$, prepared either from the double compound, $Tl_2S_2O_3,2Na_2S_2O_3,8H_2O$ (cf. Vortmann and Padberg, A., 1890, 12), and bismuth chloride or from potassium bismutho-thiosulphate and a thallous salt, forms a sparingly soluble, microcrystalline, yellow powder. It is moderately stable in neutral solution at a low temperature, but decomposes with formation of sulphur dioxide and bismuth sulphide when gently heated, the decomposition being retarded by alcohol and accelerated by a trace of acid. The salt is soluble in excess of potassium bismutho-thiosulphate solution, yielding a clear liquid, with which alcohol forms a microcrystalline, orange-yellow precipitate containing both thallium and potassium.

*Thallous stibio-thiosulphate*, $Tl_3Sb(S_2O_3)_3$, similarly prepared, forms a white, microcrystalline powder, and is stable in a dry atmosphere, but in presence of moisture rapidly reddens, owing to formation of antimony oxysulphide: $2Tl_3Sb(S_2O_3)_3 \rightleftharpoons SbOS_2 + 4SO_2 + 3Tl_2S_2O_3$.

*Thallous arseno-thiosulphate*, $Tl_3As(S_2O_3)_3$, similarly obtained, forms a white powder and decomposes more readily than the preceding compounds, in accordance with the equations: $2Tl_3As(S_2O_3)_3 = As_2S_3 + 3Tl_2S_3O_6$, $Tl_2S_3O_6 + 2H_2O = Tl_2S + 2H_2SO_4$, and $Tl_2S + H_2SO_4 = Tl_2SO_4 + H_2S$. T. H. P.

**Density and Molecular Volume of the Oxides of Lanthanum Praseodymium, Neodymium, Samarium, and Europium** WILHELM PRANDTL (*Ber.*, 1922, **55**, [*B*], 692—694).—The densitie of the earth oxides depend greatly on their method of preparatio and on the temperature to which they have been subjected. Th nitrates when ignited give very voluminous, porous oxides whic cannot be freed from adsorbed gases and consequently have lo densities. The oxides obtained from sulphates are only deprive of the last traces of sulphur trioxide with great difficulty. Com pact oxides are most conveniently prepared from the oxalates the present series is therefore obtained by ignition of the latte in an electrically heated furnace at about 900° until constant i weight. Praseodymium sesquioxide is prepared by the reductio of the black oxide, $Pr_4O_7$, by hydrogen at 900°. The followin data are recorded :

| Oxide. | Colour. | $d_4^{15}$. | Molecular volume. |
|---|---|---|---|
| $La_2O_3$ | Pure white | 6·51 | 50·08 |
| $Pr_2O_3$ | Greenish-yellow | 6·87 | 48·01 |
| $Nd_2O_3$ | Reddish-bluish-grey | 7·24 | 46·49 |
| $Sm_2O_3$ | White with yellow tinge | 7·43 | 46·95 |
| $Eu_2O_3$ | Almost white with reddish-yellow tinge | 7·42 | 47·44 |
| $Gd_2O_3$ | Colourless | 7·407 | 48·95 |
| $Pr_4O_7$ | Black | 6·71 | |
| $Eu_2O_3$ (from the nitrate) | | 6·55 | |

H. W.

**Corrosion of certain Aluminium Alloys.** L. ROLL (*Gazzetta*, 1922, **52**, i, 79—87).—The author applies Desch's metho of investigating corrosion, in which the metal is made the positiv pole in the electrolysis of sodium chloride solution (A., 1911, i 381) to various aluminium–zinc and aluminium–magnesium alloy which were prepared in a current of hydrogen in the electri furnace.

[With MARIO FRASSINETI.]—The results obtained with th *aluminium–zinc* alloys show that *solid solutions of zinc in aluminiu* undergo corrosion in such a way that neither of the two componen exerts a true protecting action on the other. This result indicat that, although the solution pressure of the aluminium is great than that of the zinc, the phenomenon is not electrochemical, bu purely chemical in character. Corrosion effected by means o electrolytic chlorine does not modify substantially the ratio betwee the weights of the disintegrated metals remaining adherent an those dissolved or precipitated when the alloys are treated wit either sea-water or sodium chloride solution. The results obtaine are fully confirmed by micrographic investigation of the corrode alloys.

[With MARIO BULLI.]—Two magnesium–aluminium alloys con taining (1) 5·68% Mg and 93·3% Al and (2) 6·9% Mg and 92·18% Al, with small proportions of iron, silica, and carbon, were examine the latter undergoing the more rapid corrosion. In either case, voluminous precipitate, mostly aluminium hydroxide, was forme and the proportion of magnesium removed was greater than th

of the aluminium. The protective action of the adherent stratum of aluminium hydroxide exerts an important influence on the course of the corrosion, rendering it discontinuous. T. H. P.

**Solubility of Aluminium Nitrate Crystals in Solutions of Nitric Acid of Various Strengths at Various Temperatures.** LOWELL H. MILLIGAN (*J. Amer. Chem. Soc.*, 1922, **44**, 567—570).—The solubility of the ennea-hydrate of aluminium nitrate has been determined in nitric acid of concentrations varying from 4·98% to 72·4% at 0·4°, 20°, 40°, and 60°. The solubility increases with increasing temperature for constant nitric acid concentration, and for the same temperature decreases rapidly with increasing nitric acid concentration. J. F. S.

**The Electrochemical Behaviour of Alloys of Manganese with Copper, Nickel, Cobalt, and Iron.** G. TAMMANN and E. VADERS (*Z. anorg. Chem.*, 1922, **121**, 193—208).—The mixed crystals of manganese with other metals show the following limiting concentrations for the action of chemical reagents and in their electrochemical behaviour: Au–Mn 0·50 mol. Au. Ag–Mn 0·75 mol. Ag. Cu–Mn 0·50 mol. Cu. Ni–Mn 0·50 mol. Ni. Co–Mn 0·50 mol. Co. Fe–Mn none. The manganese employed was not pure, and therefore these limits are only approximate. More silver (0·75 mol.) is necessary to protect the manganese than the more positive metal copper (0·5 mol.). This limit in the case of silver holds for precipitation of metals as well as for the potential of the alloys.

In the case of copper, however, a sharp limit for the action of chemical reagents could not be obtained, but the potential showed a sudden change at the concentration 0·5 mol. Cu, and the decomposition potential of the element $Cu|MnCl_2|Mn_xCu_{1-x}$ is independent of the composition of the alloy when $x<5$; with $x>5$ it decreases with decreasing amount of copper to zero. The same applies to the nickel and cobalt alloys. In the case of nickel–manganese alloys a sharp limit (0·5 mol. Ni) is found for the evolution of hydrogen from hydrochloric acid, and for the precipitation of cadmium from cadmium chloride solutions; this limit does not exist in the case of the cobalt–manganese alloys. Iron is the least able to protect the manganese in these alloys. W. T.

**Preparation of Green Manganous Sulphide.** FRIEDRICH L. HAHN (*Z. anorg. Chem.*, 1922, **121**, 209—210).—For the preparation of the green sulphide the following procedure is necessary. One hundred grams of manganese sulphate are dissolved in 300 c.c. of water. One hundred c.c. of 20% ammonia solution are saturated with hydrogen sulphide, and another 100 c.c. of the ammonia added (colourless ammonium sulphide). Thirty c.c. of this are saturated with sulphur at the boiling temperature and then made up to 100 c.c. with the colourless solution (yellow ammonium sulphide). To a boiling mixture of 5 c.c. of the manganese solution, 20 c.c. of 20% ammonia, and 100 c.c. of water, are added 30 c.c. of the yellow ammonium sulphide. The precipitated manganese sulphide

s dark green. To this is immediately added the colourless and yellow ammonium sulphide and the warm manganese salt is added n portions, the mixture being kept almost boiling and well stirred. If the manganese salt is added too rapidly, the flesh-coloured sulphide separates. W. T.

**Structure and Simple Displacement of Iron.** O. MÜGGE (*Z. anorg. Chem.*, 1921, **121**, 68—72).—In previous papers (*Jahrb. Min.*, 1899, **2**, 63; 1901, **14**, 314), it was shown that ordinary (α) iron could not possess a plane-centred cubic structnre. It is now shown, in keeping with the measurements of Westgren and Lindh (this vol., ii, 152), that the simple displacement of iron is in keeping with a space-centred cubic structure. The simple displacement which accompanies the working of α-iron is impossible in γ-iron above the transition point. Consequently, the behaviour of α-iron on working is quite different from that of γ-iron. A characteristic feature of the simple displacement in the working of α-iron is a relatively large increase in volume, which may amount to two-thirds. This is due to the formation of relatively wider concave channels. J. F. S.

**The Colour of Ferric Oxide.** J. ARVID HEDVALL (*Z. anorg. Chem.*, 1922, **121**, 217—224).—The colour of ferric oxide may vary from bright yellow to bluish-black. The light-coloured variety is obtained by the cautious heating of any of the sulphates of iron; the darker varieties are obtained by heating any of the other compounds of iron. The sulphate also gives the darker variety on heating with a flux or alone at 650°. When heated at 650—1000°, all the varieties become brown or dark violet; above 1000°, they become black or bluish-black (the colour of specular iron ore). Heating at above 650° causes a permanent change in colour. These varieties are explained either by the assumption of the existence of several stable modifications of ferric oxide or by that of different crystalline forms of the same modification. The author examined specimens of ferric oxide prepared by twenty-seven different methods; they were all crystalline. The bright yellow variety consisted of thin plates, the others were small grains or short prisms. They all gave the same *X*-ray spectrum, and therefore belong to the same system. The change from the light yellow to the darker variety was studied; it took place at 700°, the leaflets losing their form and becoming granular. W. T.

**Cobalt-Tungsten Alloys.** KARL KREITZ (*Metall u. Erz*, 1922, **19**, 137—140).—In the cobalt–tungsten series there is evidence of the formation of two compounds, $Co_6W$, melting at 1500° and CoW, melting at 1650°. Between 0 and 40% of tungsten, the alloys consist of a series of mixed crystals; from 40—70% of tungsten, of a mixture of eutectic and mixed crystals or of eutectic and the alloy CoW, according as the tungsten is less or more than 45%. The eutectic contains 44·5% of tungsten and melts at 1480°. Addition of tungsten to cobalt rapidly increases the hardness and brittleness and reduces the specific electrical

conductivity. Up to 3% of tungsten the alloys are more readily attacked by sulphuric acid than is cobalt; with more than 3% the resistance of the alloys to attack by acids rapidly increases. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] A. R. P.

**The Hydrolysis of the Roseocobaltic Salts.** P. JOB (*Compt. rend.*, 1922, **174**, 943—946).—By a quantitative application of the method previously described (this vol., ii, 301), using an oxygen electrode, the author has shown that, under the influence of hydroxyl ions, the roseocobaltic salts are converted into hydroxo-salts and that the equilibrium constant of this reaction at 16° is $6 \times 10^{-10}$. The constant of hydrolysis of the roseo-ion is calculated as being $1{\cdot}2 \times 10^{5}$. W. G.

**Electrolytic Reduction of Chromic Chloride to the Bivalent State.** M. C. TAYLOR, W. A. GERSDORFF, and E. J. TOVREA (*J. Amer. Chem. Soc.*, 1922, **44**, 612—614).—When chromic chloride solution is electrolysed in a two-compartment cell between a spiral spongy lead cathode and five graphite anodes, it is reduced to chromous chloride. With a total cathode surface of 1·24 $(dcm.)^2$ and a current of 1·6 amperes, a current efficiency of 96% may he obtained over the period required to reduce 87% of the chromium, if the solution is kept stirred and if the current is reduced when hydrogen commences to be evolved. With a steady and unchanged current strength the efficiency is only 53% for the same amount of reduction. J. F. S.

**Normal Chromium Azide and the Formation of Complex Salts.** E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1922, **52**, i, 112—115).—The compound $CrN_9,3C_6H_5N$, the behaviour of which indicates it to be a complex salt of the formula $\left[Cr \begin{smallmatrix}(N_3)_3 \\ (C_6H_5N)_3\end{smallmatrix}\right]$ (cf. A., 1919, ii, 468), may be obtained in better yield and purer condition by concentrating in a vacuum an alcoholic solution of chromium azide containing pyridine in solution.

*Chromium azide*, $Cr(N_3)_3$, prepared by prolonged treatment of an absolute alcoholic solution of crystallised chromium nitrate with anhydrous sodium sulphate and evaporation of the filtered liquid with the calculated proportion of sodium azide in a vacuum, forms a highly hygroscopic, dark green, amorphous mass. If the alcoholic solution of the chromium azide is not thoroughly dry, partial hydrolysis occurs, with formation of the basic azides, $OH{\cdot}Cr(N_3)_2$ and $CrN_3(OH)_2$.

The *compound* $CrN_9,3NaN_3$ forms green crystals, with ammonia yields a blue coloration and with silver nitrate, not silver azide, but a highly explosive complex salt, so that it evidently contains a complex anion, $[Cr(N_3)_6]'''$, analogous to $[Cr(CN)_6]'''$ and $[Cr(SCN)_6]'''$. The corresponding free acid, $H_3CrN_{18}$, could not be isolated owing to its ready decomposability. T. H. P.

**New Views on the Constitution of the Chromic Acid.** N. R. DHAR (*Z. anorg. Chem.*, 1921, **121**, 99—102).—A theoretical [paper] in which the author considers the behaviour of chromic

acid in solution. It is suggested that chromic acid is an acid of medium strength, and that it dissociates in the two stages $H_2CrO_4 \rightleftharpoons H^{\cdot}+HCrO_4'$, $HCrO_4' \rightleftharpoons H^{\cdot}+CrO_4''$, but the dissociation constant of the first stage is extremely large in comparison with that of the second stage. Similar behaviour is found in the case of maleic and dipropyl malonic acid. J. F. S.

**The Preparation of Gaseous Metallic Hydrides from Alloys and Solutions.** FRITZ PANETH, ADOLF JOHANNSEN, and MAX MATTHIES (*Ber.*, 1922, **55**, [*B*], 769—775).—The gaseous hydrides of bismuth (A., 1919, ii, 67—68) and tin (A., 1920, ii, 41) have been obtained by melting the respective metals with magnesium and decomposing the products so formed with dilute acids. The yields, however, are very small and uncertain. Numerous attempts have therefore been made to find more favourable conditions for the formation of the alloys, but these have not resulted in any improvement in the preparation of the hydrides, and have led the authors to the conclusion that the process cannot be regarded as a simple decomposition of the magnesium bismuthide or stannide. Evidence in favour of this view is found in the observation that the relatively best yields of hydride are obtained from those portions of the mixtures in which the magnesium and tin or bismuth have not been melted together completely, that bismuth hydride is obtainable from magnesium which is merely coated with fused metallic bismuth, that the well-defined compounds, $Na_3Bi$ and $Na_4Sn$, do not give a trace of metallic hydride, and, in particular, that thorium-*C* deposited on magnesium foil continues to evolve the metallic hydride for a long time after removal of the thin film is complete. It therefore appears possible to obtain metallic hydrides from suitable solutions of the metals instead of from their alloys and, in this connexion, the production of tin hydride by the action of magnesium on a solution of tin sulphate is described in detail; the operation proceeds with such uniformity and gives such good yields that it is suitable for lecture demonstration purposes. A solution of stannous chloride in hydrochloric acid may replace that of tin sulphate, but, in this case, the deposit formed when the gas is led through the heated Marsh tube consists of colourless stannous chloride (due to the hydrogen chloride carried forward in the gas) instead of metallic tin. This possibly accounts for the previous non-observance of the formation of tin hydride when tin is used for evolving hydrogen in Marsh's test for arsenic. H. W.

**The Preparation of Gaseous Metallic Hydrides by the Spark Discharge.** FRITZ PANETH, MAX MATTHIES, and EDGAR SCHMIDT-HEBBEL (*Ber.*, 1922, **55**, [*B*], 775—789).—Attempts are described to produce bismuth hydride by passing active hydrogen over bismuth powder, but the gas is not formed in identifiable amount. Small quantities of it are produced when rods of bismuth are used as electrodes in the formation of active hydrogen. Better results are obtained by the analogous use of lead, and the further experiments are mainly performed with this metal. The

yields with the disposition of apparatus outlined above are sm and very irregular, in spite of the apparent uniformity in t conditions, but some improvement can be effected by using fine divided lead or, preferably, granulated lead packed round t platinum electrode and arranging the tube (it is figured a described fully in the original) in such a manner that the hydri produced is removed rapidly from the neighbourhood of t discharge. Even under these conditions, the experiments a very uncertain, and the yields of hydride are found to dimini with increasing purity of the reagents, thus indicating that sor impurity is functioning as catalytic accelerator. Systematic sear has shown that methane and the vapours of ethyl alcohol, eth ether, glycerol, light petroleum, paraffin, and the pyrogenic vapou from caoutchouc and paper have a very marked positive actio On the other hand, mercury, oxygen, iron, iodine, sulphur, sulph dioxide, hydrogen sulphide, silicon hydride, ammonia, arsine, a stibine have no appreciable effect. Subsequent experiments a therefore performed in general with the addition of coal gas whi is purified by successive treatment with concentrated sulphuric aci alkaline sodium hyposulphite solution, potassium hydroxide (50% calcium chloride, and phosphorus pentoxide. The arrangement the apparatus is sketched and described in detail in the origina The product, which is condensed by liquid air, contains the metall hydride mixed with a relatively large excess of hydrocarbons the products derived from them under the action of the electr discharge, and the mixtures cannot be approximately separat by any available process of fractionation. It is therefore necessa to elaborate a method for the analysis of minute amounts of metall hydride in the presence of an indefinite mixture of hydrocarbon This is effected by decomposing the hydride by heat and measur ment of the pressure of the resultant gases; the latter are cool by liquid air, whereby only the hydrogen remains in the gaseo condition, and this is then absorbed by a heated palladium capillar The pressure of residual gas is then estimated under the san conditions as previously, the difference in the readings giving t amount of hydrogen. The deposit of metal is weighed. T method gives satisfactory results with stibine and with tin hydrid to which the formula, $SnH_4$, is assigned. With lead hydride it unsatisfactory, since this substance cannot be separated by fra tionation from unsaturated hydrocarbons, which subsequent become hydrogenated by the hydrogen derived from the hydride.

Under the experimental conditions adopted, volatile hydrid are formed from lead, bismuth, tin, antimony, tellurium, germaniu arsenic, and selenium, but not from aluminium, zinc, or mercury.

H. W.

# Mineralogical Chemistry.

**New Hypothesis of the Origin of Natural Fuels.** G. CALCAGNI (*Gazzetta*, 1922, **52**, i, 87—93).—The author advances and discusses the view that coal, natural graphite, petroleum, etc., may have had their origin in organic compounds, even of great complexity, existing on the earth long prior to the appearance of life.

T. H. P.

**The Constitution of Anthracite.** ARTHUR GROUNDS (*J. Soc. Chem. Ind.*, 1922, **41**, 88—93T).—Three constituents can be recognised in anthracitic coals, namely fusain, occurring to the extent of about 1% or less, a glossy constituent similar in appearance to the vitrain of bituminous coals and designated $\psi$-vitrain, which forms the major portion of the seams, and a constituent similar to the clarain of bituminous seams present to the extent of 5—10% at most in the anthracites examined. The fusain was generally soft, porous, and pulverulent, and could be separated from the other constituents by fractional sieving. In certain cases, a harder variety was found associated with the soft fusain, and this contained a higher percentage both of ash and of volatile organic matter than the latter. Whilst the fusain in bituminous seams usually contains less volatile organic matter than the associated coal, the anthracitic fusain sometimes contains more and sometimes less. In one case, the dense fusain contained 23·22% compared with 11·60% for the adjacent $\psi$-vitrain, calculated on a moisture- and ash-free basis. The ash of fusain varies widely from about 3·0—15·0% and is much higher than the ash of $\psi$-vitrain, which usually varies from 0·1 to 1·5%. The water-soluble constituent of the ash of $\psi$-vitrain amounts to 1·7 to 6·9% of the total, and thereby differs widely both from that of vitrain, which usually contains about 70% of water-soluble substance, and of fusain, which varies from 10 to 50%. This variation with fusain is doubtless due to its porous nature, which allows the percolation of saline solutions which deposit their solid matter in the fusain on being subjected to concentration by heat. In all the seams examined, the $\psi$-vitrain gives an almost constant $Al_2O_3 : SiO_2$ ratio of 1·10, very similar to that of the fusain examined by the author (1·17), but very different from that of the ordinary vitrain of bituminous seams (2·55).

G. F. M.

**Some Constituents of Lignites. II.** R. CIUSA and M. CROCE (*Gazzetta*, 1922, **52**, i, 125—128; cf. A., 1921, ii, 343).—The various natural organic compounds found in lignites may be grouped, according to their melting points, in the following classes: (1) fictelite, m. p. 46°; dinite, m. p. 35°; and scheerite, m. p. 44°; (2) simonellite, m. p. 62°; (3) konleinite, m. p. 108—114°; (4) branchite, m. p. 75—81°; bombiccite, m. p. 75°; hartite, m. p. 75°; the hydrocarbon of Terni lignite (*loc. cit.*), m. p. 75°, and hofmannite, m. p. 71°.

The authors find that, when purified, all the substances of group (4), as well as mixtures of them, have m. p. 74—75°, and all have compositions and molecular weights corresponding with the formula $C_{20}H_{34}$.

The dihydrocamphene, $C_{20}H_{34}$, m. p. 74—75°, obtained by Étard and Méker (A., 1898, i, 443), and by Houben (A., 1906, i, 21), has been prepared by various methods and is found to have m. p. 85—86° (cf. Hesse, A., 1906, i, 375), its mixture with hartite having m. p. 52°. T. H. P.

**Fossil Wax of Monte Falò.** R. Ciusa and R. Vois (*Gazzetta*, 1922, **52**, i, 135—136).—This wax, m. p. 47—49° (crude), 50—52° (purified), contains the paraffin hydrocarbons $C_{23}H_{48}$, $C_{24}H_{50}$, and $C_{26}H_{54}$, together with higher members of the series, and is free from compounds containing sulphur or oxygen. T. H. P.

**Stasite, a New Mineral Dimorphous with Dewindtite.** Alfred Schoep (*Compt. rend.*, 1922, **174**, 875—877).—As a dirty yellow material, this occurs mixed with torbernite at Kasolo, Katanga, Belgian Congo. Under the microscope, it is seen to consist of minute, flattened prisms of a golden-yellow colour and with straight extinction, *d* 5·03. In the oxidising flame it fuses to a black globule, and it is soluble in nitric acid to a yellow solution. The extremes of several analyses made on two lots of material dried at 100° are given under I (also CaO 0·30, MgO trace).

| | PbO. | $UO_3$. | $P_2O_5$. | Ign. | $H_2O$. | Insol. |
|---|---|---|---|---|---|---|
| I. | 25·53—26·20 | 55·77—56·28 | 10·32—10·60 | 6·24—6·71 | 5·60 | 0·40—1·17 |
| II. | 26·40 | 57·19 | 10·68 | — | 5·70 | — |

The mean values calculated to 100% given under II correspond with the formula $4PbO,8UO_3,3P_2O_5,12H_2O$, identical with that for dewindtite (this vol., ii, 305). The new mineral is thus dimorphous with dewindtite, differing from it in colour, density, and form of the crystals. L. J. S.

**Aphthitalite from Kilauea.** H. S. Washington and H. E. Merwin (*Amer. Min.*, 1921, **6**, 121—125).—On the walls of hot (about 800°) crevices in new lava are bright blue encrustations of small, hexagonal plates of aphthitalite, which on cooling become nearly white. In cooler parts of the crevices the encrustation consists of thenardite. The aphthitalite is optically uniaxial with $\omega$ 1·487, $\epsilon$ 1·492; analysis gave

| $SO_3$. | Cl. | $K_2O$. | $Na_2O$. | CaO. | CuO. | $H_2O$. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|
| 51·50 | 0·03 | 23·72 | 22·76 | 0·39 | 0·46 | 0·25 | 0·76 | 99·87 |

corresponding with $K_2SO_4$ 43·88, $Na_2SO_4$ 52·12, or $K_2SO_4 : Na_2SO_4$ about 1 : 1·5. The variable composition of aphthitalite and its relation to arcanite (orthorhombic $K_2SO_4$) are discussed. Anhydrous copper sulphate crystallised from hot sulphuric acid is orthorhombic (pseudo-hexagonal) with $\beta$ 1·72 and $\gamma - \alpha$ 0·02, and is thus related crystallographically to the alkali sulphates. The alkalis and copper were probably volatilised as sulphides, which in contact with the air are deposited as sulphates. L. J. S.

**A Tantalate and Columbite from South Dakota.** WILLIAM P. HEADDEN (*Amer. J. Sci.*, 1922, [v], **3**, 293—299).—Analyses of fragments of brown or greyish-black columbite: I—III, from the Old Mike mica mine in Custer Co.; IV, from Harney City, Pennington Co.; V and VI, from Tin Mountain, Custer Co. Fragments of a black tantalate (presumably tapiolite) gave VII—XIII. Crystals determined to be tapiolite from Prospect (near the Old Mike mica mine) gave XIV.

| | $Cb_2O_5$. | $Ta_2O_5$. | $TiO_2$. | $SnO_2$.* | FeO. | MnO. | Total. | *d.* |
|---|---|---|---|---|---|---|---|---|
| I. | 68·00 | 9·88 | 0·53 | 0·88 | 5·45 | 14·79 | 99·53 | 5·201 |
| II. | 67·20 | 10·10 | 0·92 | 0·96 | 5·96 | 15·08 | 100·22 | 5·421 |
| III. | 63·90 | 13·74 | 0·80 | 0·54 | 5·92 | 14·95 | 99·85 | 5·496 |
| IV. | 34·60 | 46·02 | 1·52 | 0·38 | 13·32 | 4·31 | 100·15 | 6·444 |
| V. | 27·22 | 53·47 | 1·30 | 0·44 | 11·91 | 5·66 | 100·00 | 6·725 |
| VI. | 28·81 | 53·67 | 1·63 | 0·38 | 12·00 | 5·20 | 100·69 | 6·845 |
| VII. | 8·63 | 69·55 | 1·50 | 5·29 | 10·84 | 4·19 | 100·00 | 6·954 |
| VIII. | 5·49 | 76·08 | 2·84 | 0·22 | 14·16 | 1·21 | 100·00 | 7·019 |
| IX. | 6·07 | 77·24 | 0·81 | 1·18 | 13·60 | 1·02 | 100·82 | 7·180 |
| X. | 5·56 | 78·28 | 1·33 | 0·28 | 13·35 | 1·22 | 100·62 | 7·468 |
| XI. | 4·32 | 79·50 | 0·92 | 0·32 | 13·42 | 1·56 | 100·04 | 7·794 |
| XII. | 3·69 | 81·40 | 0·58 | 0·12 | 12·55 | 1·73 | 100·07 | 7·878 |
| XIII. | 1·97 | 83·57 | trace | 0·10 | 13·28 | 1·19 | 100·10 | 7·975 |
| XIV. | 5·18 | 77·23 | 1·38 | 0·32 | 14·84 | 0·42 | 100·00 | 7·190 |

* Including some $WO_3$; small amounts of cassiterite have been deducted.

From these analyses it is seen that with increasing tantalic acid, not only is there an increase in density, but also iron replaces manganese.
L. J. S.

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## Analytical Chemistry.

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**Xylenol-blue and its Proposed Use as a New and Improved Indicator in Chemical and Biochemical Work.** ABRAHAM COHEN (*Biochem. J.*, 1922, **16**, 31—34).—The author recommends as an indicator *5-hydroxy*-1 : 4-*dimethylbenzenesulphonephthalein* (xylenol-blue), which has an acid range from $P_H$ 1·2 (red) to $P_H$ 2·8 (yellow), and an alkaline range from $P_H$ 8·0 (yellow) to $P_H$ 9·6 (blue). This new indicator possesses several advantages over thymol-blue, in place of which it can he successfully employed.
W. O. K.

**Influence of Ethyl Alcohol on the Colour Change of Phenolphthalein.** RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1922, **100**, 532—536).—It is shown that the presence of alcohol in acidimetric titrations increases the amount of alkali necessary to produce a colour change with phenolphthalein as indicator. The cause of the slight increase is discussed and it is shown to be probable that a combination of the alcohol with the phenolphthalein explains the experimental results. (Cf. Hildebrand, A., 1909, ii, 25).
J. F. S.

**The Application of the Iodine Electrode in Potentiometric Titrations.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 172—191).—When an iodine electrode is used for the titration of an iodide by means of silver nitrate, it is found that in a neutral solution an error of 0·8% occurs, probably due to adsorption. In a solution containing free sulphuric acid the error is negligible, although the potential requires a considerable time to reach constant value. By means of the iodine electrode, an iodide may be titrated with silver nitrate in presence of an equivalent quantity of bromide or twenty times the equivalent of chloride. Mercuric perchlorate is a suitable reagent for accurate titration of iodides; mercuric nitrate in nitric acid solution is useless, as the acid oxidises a portion of the iodide. By using the perchlorate, a quantity of iodide as small as 0·6 mg. may be estimated with accuracy; good results are obtained in presence of an equivalent quantity of bromide or a large excess of hydrochloric acid.

Mercuric chloride may be estimated accurately by the potentiometric method by using the iodine electrode. Other metals have been investigated from this point of view, and it is found that the method is applicable to thallous salts, probably to palladium and some other rare metals, but not to lead or bismuth. H. J. E.

**Hydrated Oxalic Acid as an Oxidimetric Standard.** ARTHUR E. HILL and THOMAS M. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 546—557).—The trustworthiness of crystallised oxalic acid as a standard in oxidation processes has been investigated. It is shown that crystals of hydrated oxalic acid as usually prepared from aqueous solution contain several tenths per cent. of included water, which is not entirely lost by four months' exposure to atmospheres of the same aqueous tension as the crystals or higher. Crystals superficially dry will lose this included water in about twenty-four hours if ground to pass a 100-mesh sieve and set in an atmosphere of an aqueous tension in equilibrium with the hydrate. A mixture of the hydrated and anhydrous oxalic acid is the only desiccating agent giving an aqueous tension in equilibrium with the hydrate at all temperatures. The powdered hydrate can be dried in about an hour in a current of air passed over this desiccating agent, so that its oxidimetric value agrees with that of sodium oxalate within 0·025%. J. F. S.

**Pipettes.** VERNEY STOTT (*J. Soc. Glass Tech.*, 1921, **5**, 307—325).—Pipettes should be adjusted for a particular time of delivery, and when testing pipettes it is important to record both the time of delivery and the capacity. The time required for the delivery of the contents of the pipette should be within certain limits, since pipettes are untrustworthy if the time of delivery is too short and also if it is too long. A definite time should be allowed for drainage when graduating, testing, or using pipettes. W. P. S.

**Device for the Removal of Fumes.** M. FISCHLER (*Chem. Zeit.*, 1922, **46**, 224).—A device for the removal of fumes during the oxidation of organic substances with sulphuric and nitric acids

consists of a wide earthenware or sheet-iron tube which is bent so as to enter the flue of a fume chamber; the lower end of the tube is provided with a small siphon trap whilst a wide side-tube receives the neck of the flask in which the material is being treated. A tubulure on the side tube admits the bent stem of a tapped funnel so that further quantities of acid may be added to the flask when necessary. The upper end of the tube may be slotted to receive a burner which aids the draught. W. P. S.

**Detection of Oxygen in Organic Compounds.** JEAN PICCARD (*Helv. Chim. Acta*, 1922, **5**, 243—244).—It is suggested that the fact that solutions of iodine in solvents free from oxygen are blue, but brown in alcohol, ether, or acetone, can form the basis of a method for the qualitative detection of oxygen in organic compounds. Since the brown colour depends on the formation of an additive compound with the oxygen atom, iodine in excess of this requirement must be avoided. Thus, although benzene containing 2% of ether dissolves iodine with a colour scarcely distinguishable from that obtained with pure benzene, a distinct brown colour is observable on the addition of the same proportion of ether to a solution (almost colourless) of iodine in one million parts of benzene if a layer 90 cm. deep be examined. J. K.

**Clinical Method for the Estimation of Chlorides in Blood.** HERMAN FRIEND (*J. Biol. Chem.*, 1922, **51**, 115—119).—For clinical purposes, plasma and not whole blood should be used for chloride estimations. In the method described, the plasma is separated immediately to prevent alterations in the distribution, precipitated by shaking with alumina cream, and chlorides estimated in the filtrate by titration with silver nitrate. E. S.

**Catalytic Analyses. I. Estimation of Chloric Acid.** SHIN-ICHIRÔ HAKOMORI (*J. Chem. Soc. Japan*, 1922, **43**, 62—70).—This method is based on the fact that the ferrous-ion acts as a catalyst in the reaction between chloric acid and hydriodic acid (Green, *J. Physical Chem.*, 1908, **12**, 389). To a solntion containing approximately potassium iodide 10%, ferrous ammonium sulphate 3%, and 0·2% of the sample, about $3N$-hydrochloric acid is added, and after ten to fifteen minutes the mixture is titrated with sodium thiosulphate solution. K. K.

**The Estimation of Total Sulphur in Urine.** ROBERT ROBISON (*Biochem. J.*, 1922, **16**, 134—136).—Sulphur can be best estimated in the urine by a modification of Benedict's method. 2·5 C.c. of a solution of copper nitrate (40 grams) and copper chloride (15 grams) in water (100 grams) are added to the urine (10 c.c.) and the mixture is evaporated to dryness, and then heated over a plate or small flame to oxidise the sulphur. After being heated for a further twenty minutes, the residue is dissolved in $2N$-hydrochloric acid (10 c.c.) and diluted with distilled water (300 c.c.). The oxidised sulphur is then estimated as barium sulphate.
W. O. K.

**Analysis of Chlorosulphonic Acid.** G. WEISSENBERGER and A. ZODER (*Z. anal. Chem.*, 1922, **61**, 41—48).—Volumetric methods, which depend on the estimation of the total acidity of the sample (after suitable dilution) and subsequent titration of the hydrochloric acid, yield untrustworthy results owing to the fact that the large quantity of sulphate ions present interferes with the titration of the chloride by Mohr's or Volhard's methods. The quantity of chlorosulphonic acid and of free sulphuric acid found is too high and the sulphur trioxide is too low. Gravimetric methods yield correct results for the hydrochloric acid and the sulphuric acid. Fairly correct results are also obtained by distilling the sample and collecting the portion which has b. p. 154—156°. W. P. S.

**Estimation of very small Quantities of Injurious Acids in Air.** G. LAMBRIS (*Z. anal. Chem.*, 1922, **61**, 20—40).—Flue gases may contain *sulphuric*, *sulphurous*, and *hydrochloric acids*, which, when allowed to escape into the atmosphere, may have an injurious effect on vegetation. A method for the estimation of these acids consists in passing the air at the rate of about 100 litres per hour for two or three hours through an absorption vessel packed with cotton wool moistened with water and then through a second vessel containing cotton wool moistened with hydrogen peroxide. The sulphuric and hydrochloric acids are absorbed in the first vessel, whilst the sulphurous acid is absorbed and oxidised to sulphuric acid in the second vessel. The contents of the vessels are subsequently titrated and the quantities of the different acids estimated in the usual way. About 10% of the sulphurous acid is retained in the first vessel; this may be removed and conveyed over into the second vessel by means of a current of air free from acidity, or its quantity may be estimated by neutralising the contents of the vessel, using methyl-orange as indicator, then adding hydrogen peroxide, and titrating the sulphuric acid formed by the oxidation of the sulphurous acid. The method is suitable for the estimation of 1 part of acid per 500,000 parts of air.

W. P. S.

**Estimation of Sulphate-ion as Barium Sulphate I.** K. P. CHATTERJEE (*Z. anorg. Chem.*, 1922, **121**, 128—134).—The author carried out the precipitation under various conditions. The amount of hydrochloric acid added to make the precipitate granular and easily filtered should not exceed 0·1% of the volume of the liquid. Excess of barium chloride is not as detrimental as an excess of hydrochloric acid provided the precipitate is well washed. Rapid precipitation results in a stronger adsorption of the mother-liquor than slow precipitation. Dry barium sulphate gives up the adsorbed chloride more readily than the wet salt.

W. T.

**Cathodic Deposition of Tellurium and Selenium from their Oxy-acids and their Electroanalytical Estimation.** ERICH MÜLLER [with MENZEL and SCHUBERT] (*Z. physikal. Chem.*,

1922, **100**, 346—366).—The detection of selenium and tellurium may be effected as follows: (*a*) selenium:—2 c.c. of the solution containing selenium is treated with 3 drops of concentrated sulphuric acid and a few small crystals of hydrazine sulphate and heated. A red coloration or precipitate indicates the presence of selenium. This reaction is sensitive to 5 mg. of selenium per litre; (*b*) tellurium:—1 c.c. of solution with 1 c.c.of concentrated ammonia and a few crystals of hydrazine sulphate when boiled give a brown coloration or precipitate if tellurium is present. This reaction is sensitive to 10 mg. of tellurium per litre; (*c*) selenium and tellurium in the same solution:—3 c.c. of solution are treated with 3 drops of concentrated sulphuric acid and a little hydrazine sulphate and boiled, a red coloration of selenium results; this is filtered, the filtrate made alkaline with ammonia, more hydrazine sulphate added, and the solution again boiled; a brown coloration indicates tellurium; (*d*) selenious acid in the presence of selenic acid:—3 c.c. of the solution are treated with 5 c.c. of concentrated sulphuric acid and a little sodium sulphite and boiled; a red precipitate or coloration indicates selenious acid. The reaction is sensitive to 5 mg. of selenium per litre. After filtration, 3 c.c. of concentrated hydrochlorie acid and more solid sodium sulphite are added and the solution is boiled; a red precipitate or coloration indicates selenic acid; the sensitiveness is the same as above; (*e*) tellurous acid in the presence of telluric acid: these two acids cannot be detected in the presence of one another by simple reduction, since both acids are reduced, although at different rates. On electrolysis in sulphuric acid solution, the tellurous acid alone is reduced, and when this is complete the solution is concentrated and boiled with hydrochloric acid and sodium sulphite, when a brown precipitate or coloration indicates telluric acid. The cathodic decomposition potential of tellurous acid in 2*N*-sulphuric acid is −0·08 volt. No deposition potential could be obtained for tellurium from a 2*N*-sulphuric acid solution of telluric acid, from which it follows that tellurium cannot be deposited from telluric acid. A simple decomposition potential could not be observed for selenium from selenious acid, although selenium was seen to be deposited at about 0·05 volt, but the first selenium deposited appears to act as an insulating diaphragm and prevents further deposition; when the voltage is raised so that hydrogen is liberated, the selenium leaves the electrode in flakes. On adding copper sulphate to the sulphuric acid solution of selenious acid, the selenium and copper are deposited together in a conducting form at +0·15 volt, so that all the selenium may be deposited at this potential. Selenium cannot be electrolytically deposited from selenic acid on platinum either at 20° or 80°. Tellurium in tellurous acid may be quantitatively estimated as follows. A maximum weight of 0·25 gram of tellurous acid is dissolved in 175 c.c. of 2*N*-sulphuric acid and electrolysed for two and a half hours between two platinum Winkler electrodes which are connected directly with a single lead accumulator. The solution must be rapidly stirred during the electrolysis. The deposit, which is uniformly dense and grey, is washed with water and alcohol

and dried over sulphuric acid in a desiccator. The average erro of the method is $\pm 0.1\%$. Tellurous acid may be estimated i the presence of telluric acid by this method, and after the telluriun from the tellurous acid has been removed the solution is boile with hydrochloric acid to reduce the telluric acid to tellurous acid and the estimation of this then carried out as before. Seleniun may be estimated in selenious acid as follows. A quantity o selenious acid containing not more than 0·07 gram of seleniun is dissolved in $2N$-sulphuric acid and mixed with a quantity o copper sulphate in $2N$-sulphuric acid such that the concentratio of copper is four times that of the selenium, and electrolysed fo two hours at the ordinary temperature with rapid stirring betwee two Winkler platinum electrodes which are connected directl with a single lead accumulator. The deposit of copper an selenium is washed with water and alcohol and carefully dried The weight of the copper is known from the amount of coppe sulphate solution used. The method is good, but suffers in accurac on account of the small amount of selenium which may be use in a determination. Several attempts are described which wer designed for the estimation of selenious acid in the presence o tellurous acid, but all failed to give the desired result. J. F. S.

**The Estimation of Nitrogen in Nitric Esters.** H. KESSELER R. RÖHM, and G. LUTZ (*Z. angew. Chem.*, 1922, **35**, 145).—Th esters are saponified at 40—50° with aqueous potassium hydroxid (1 : 1), the nitrates and nitrites so obtained reduced to ammoni with Devarda's alloy (50% copper, 45% aluminium, and 5% zinc), and the ammonia distilled into $N/10$-sulphuric acid and titrated back with $N/10$-sodium hydroxide with methyl-red as indicator. The method is specially recommended for nitro-starches, to which other rapid methods cannot be applied. H. C. R.

**Colorimetric Estimation of Phosphorus.** LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 60—62).—The method developed by the author (cf. Namias, *Stahl und Eisen*, 1890) is based on the observation that treatment of ammonium phosphomolybdate with hot sodium thiosulphate solution yields a liquid coloured intensely blue owing to the formation of molybdenum compounds which have not been identified. The optimum conditions have been fixed and two colorimeters designed, one for low and the other for moderately high percentages of phosphorus. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] T. H. P.

**A Rapid Colorimetric Method for the Estimation of the Inorganic Phosphorus in Small Amounts of Serum.** FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, **50**, 329—337).—The estimation is performed on 1 c.c. of serum. Proteins are removed by means of trichloroacetic acid, and the inorganic phosphates then precipitated as strychnine phosphomolybdate by the addition of a strychnine molybdate reagent (cf. Embden, A., 1921, ii, 462). After centrifuging and washing with the minimum amount of water, the precipitate is dissolved in 1% sodium hydroxide,

diluted, and the colour produced on reduction with 20% potassium ferrocyanide and concentrated hydrochloric acid compared with a standard. The error does not exceed 5%. E. S.

**Gravimetric Estimation of Hydrogen Phosphide and a New Apparatus for Gas Analysis.** L. Moser and A. Brukl (*Z. anorg. Chem.*, 1921, **121**, 73—94).—The reactions of phosphine with solutions of iodic acid, silver nitrate, mercuric chloride, gold chloride, and copper sulphate have been investigated with the object of finding a gravimetric method for the estimation of high concentrations of phosphine. The various methods for estimating small quantities of phosphine are discussed. Phosphine containing only a few per cent. of hydrogen is best prepared by the action of 1 : 10-sulphuric acid on aluminium phosphide, and gas obtained by this method was used in all analyses described. When phosphine is led into a 2*N*-solution of iodic acid, the gas is completely absorbed, but occasionally a small amount of fog, due to the inflammable hydride, is formed; this, however, is completely absorbed in half an hour. The solution is then heated and a current of carbon dioxide passed through until all the iodine has been distilled into a solution of potassium iodide. The amount of iodine is determined by titration with thiosulphate, and the phosphoric acid left in the flask estimated as magnesium pyrophosphate. The results obtained in both cases are identical. The reaction is represented by the equation $8HIO_3+5PH_3=5H_3PO_4+4I_2+4H_2O$. The error is a little more than 0·1%. Phosphine is shown to react with excess of silver nitrate in stages according to the equations : (1) $3AgNO_3+PH_3=PAg_3+3HNO_3$; (2) $PAg_3+AgNO_3+2H_2O=H_3PO_2+4Ag+HNO_3$; (3) $H_3PO_2+2AgNO_3+H_2O=H_3PO_3+2Ag+2HNO_3$; (4) $H_3PO_3+2AgNO_3+H_2O=H_3PO_4+2Ag+2HNO_3$. The total action is therefore represented by the equation $8AgNO_3+PH_3+4H_2O=H_3PO_4+8Ag+8HNO_3$. By the action of a cold saturated solution of silver acetate added drop by drop to a vessel through which a steady stream of phosphine is added, the authors have been able to prepare *silver phosphide*, $PAg_3$. This substance is an easily oxidisable, velvety, black powder which cannot be dried without decomposition; it is not decomposed by air-free cold water, but in water containing air it decomposes into metallic silver. It is rapidly decomposed by boiling water, concentrated nitric acid, warm hydrochloric acid with the liberation of phosphine, and concentrated sulphuric acid with the liberation of sulphur dioxide. The estimation of phosphine by means of silver nitrate takes place in a closed absorptiometer which consists of a bulb (120 c.c. capacity) to the bottom of which a glass tube 10 cm. long and 3 mm. bore is attached, and to the top a capillary tube which is bent twice at right angles for connecting with a gas burette. The capillary carries a tap which, in addition to the ordinary bore, is also bored along its axis. The apparatus is placed with its lower tube in a beaker containing *N*/10-silver nitrate solution and filled with the liquid and the gas drawn in and the apparatus shaken. After fifteen minutes the liquid is all run into the beaker and the apparatus

washed with a little dilute nitric acid and water, and the washing added to the beaker. The solution is then treated with hydrochloric acid, filtered, and the phosphoric acid in the filtrate estimated as magnesium pyrophosphate. The results obtained by this method are in excellent agreement with those obtained by the iodic acid method. The substitution of an ammoniacal solution of silver nitrate for aqueous silver nitrate has no advantage, and attempts to estimate the phosphine by weighing the precipitated silver failed. A *N*/5-solution of mercuric chloride can be used as absorbent for phosphine. The method of work is the same as described for silver nitrate. The reactions taking place are given by the equations (1) $6HgCl_2+2PH_3=3HgCl_2,P_2Hg_3+6HCl$; (2) $6HgCl_2+PH_3+3H_2O=H_3PO_3+6HCl+6HgCl$; (3) $8HgCl_2+PH_3+4H_2O=H_3PO_4+8HCl+8HgCl$. When the absorption is complete the liquid and precipitate are boiled with bromine water, the mercury is removed by hydrogen sulphide, and the phosphoric acid determined as magnesium pyrophosphate. The results are uniformly good. A *N*/5-solution of gold chloride is a good absorbent for phosphine; the method employed is the same as described above. The following reactions occur during the absorption (1) $3AuCl_3+PH_3+3H_2O=3AuCl+H_3PO_3+6HCl$; (2) $4AuCl_3+PH_3+4H_2O=H_3PO_4+4AuCl+8HCl$; (3) $3AuCl+PH_3=Au_3P+3HCl$; (4) $3Au_3P+AuCl_3+6H_2O=10Au+3H_3PO_2+3HCl$; (5) $3H_3PO_2+2AuCl_3+3H_2O=2Au+3H_3PO_3+6HCl$; (6) $3H_3PO_3+2AuCl_3+3H_2O=2Au+3H_3PO_4+6HCl$. The total and completed action is represented by the equation $8AuCl_3+3PH_3+12H_2O=8Au+24HCl+3H_3PO_4$. After the action is completed, the gold in solution is precipitated by hydrogen sulphide, filtered, and the phosphoric acid in the filtrate estimated as above after oxidation by bromine water. A *N*/5-solution of copper sulphate is a good but much slower absorbent for phosphine than the other salts mentioned. The analysis, using this salt, is carried out as in the case of gold. The absorption occurs according to the equations (1) $3CuSO_4+PH_3+3H_2O=H_3PO_3+3Cu+3H_2SO_4$; (2) $4CuSO_4+PH_3+4H_2O=4Cu+H_3PO_4+4H_2SO_4$; (3) $3CuSO_4+2PH_3=Cu_3P_2+3H_2SO_4$; (4) $Cu_3P_2+3Cu=2Cu_3P$. J. F. S.

**Estimation of Krypton and Xenon in Absolute Values by Spectrophotometry.** CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1922, **174**, 908—913).—A modification of previous work (A., 1911, ii, 439, 1134). The authors have prepared mixtures of pure argon with differing amounts of pure krypton on the one hand and pure xenon on the other. For the mixtures containing krypton, the pressures at which the intensity of the line $\lambda=5870 \cdot 9$ of the krypton is just equal to that of the argon lines $\lambda=5860 \cdot 5$ and $5912 \cdot 31$ respectively have been determined for each mixture. For the xenon mixtures, the xenon line $\lambda=4671 \cdot 22$ and the argon line $\lambda=4702 \cdot 5$ have been used. These figures thus give a means of calculating the amounts of krypton or xenon in argon–krypton and argon–xenon mixtures respectively. The limits of dilution at which measurements can be made are for krypton $0 \cdot 5$—$4 \cdot 5\times 10^{-}$

and for xenon 2—$8 \times 10^{-4}$. If the mixture to be examined contains too much krypton or xenon, it must first be diluted with pure argon, but if it is too dilute it must be concentrated by fractionation, using coconut charcoal. W. G.

**Estimation of Carbon in Cast Iron and Steel by Corleis's Apparatus.** G. Batta and H. Thyssen (*Bull. Soc. chim. Belg.*, 1922, **31**, 112—117).—By means of a number of blank experiments, errors in the estimation have been traced to incomplete drying of the gas before absorption of the carbon dioxide by alkali. Detailed experimental methods based on a considerable number of analyses have been worked out and are recommended. H. J. E.

**Rapid Analysis of Potassium Perchlorate.** Victor Lenher and Martin Tosterud (*J. Amer. Chem. Soc.*, 1922, **44**, 611—612).—The following method is described as the most satisfactory for the estimation of perchlorate. A 0·5 gram sample is mixed in an agate mortar with 1·0 gram of manganese dioxide, transferred to a porcelain crucible, and heated for fifteen minutes at 600—700°. After cooling, the mass is extracted with hot water, filtered, and the chlorine determined by either Mohr's or Volhard's method. The results are about 0·2—0·3% low, due to loss by volatilisation. A blank experiment with the manganese dioxide should always be carried out. Greater accuracy is obtained by Lamb and Marden's method (A., 1912, ii, 681) of heating the perchlorate alone in a glass tube and retaining the fumes evolved with a plug of asbestos. J. F. S.

**Estimation of Sodium in Serum without the Use of Platinum Dishes.** S. J. Wilson (*J. Biol. Chem.*, 1922, **50**, 301—302).—In the estimation of sodium as pyroantimonate by Kramer and Tisdall's method (A., 1921, ii, 463), the precipitation may be carried out in tinned dishes, in place of platinum ones, without loss of accuracy. E. S.

**Effect of Hydrogen-ion Concentration on the Estimation of Calcium.** Alfred T. Shohl (*J. Biol. Chem.*, 1922, **50**, 527—536).—In the estimation of calcium in the presence of magnesium and phosphates by McCrudden's method (A., 1910, ii, 243; 1911, ii, 1136) the hydrogen-ion concentration must be kept within the limits $P_H$ 4·0 and $P_H$ 5·6. With a more acid solution, calcium oxalate dissolves, whilst with a less acid one magnesium ammonium phosphate is precipitated. E. S.

**A Rapid and Accurate Method for estimating Calcium in Urine.** Alfred T. Shohl and Frank G. Pedley (*J. Biol. Chem.*, 1922, **50**, 537—544).—Uric acid and other substances present in the urine which would interfere with the titration by permanganate are oxidised by boiling with ammonium persulphate after acidification with nitric or sulphuric acid. The calcium is then precipitated by addition first of oxalic acid and then of ammonia until neutral to methyl-red, which brings the solution to $P_H$ 4·8—5·3 (cf. preceding abstract). After remaining over-night, the precipitate is filtered

on to a hardened filter-paper, washed, transferred to the origina flask, and the calcium oxalate estimated by titration with permanganate. E. S.

**The Analytical Chemistry of Colloidal Disperse Systems. I. Estimation of Silver Ion in the Presence of Colloidal Silver.** A. GUTBIER, J. HUBER, and O. KUPPINGER (*Ber.*, 1922 **55**, [*B*], 748—752).—The method depends on the precipitation of the protected metallic colloid in reversible form by the addition of methyl alcohol and titration of the silver remaining in solution by Volhard's method. To avoid adsorption of silver ions by the precipitate, it is necessary, before precipitation, to convert the dissolved silver into the complex form, which can be most conveniently effected by means of solid ammonium carbonate.

A measured volume of the protected colloidal system, prepared at the atmospheric temperatnre and in the dark, is agitated with a corresponding excess of pure solid ammonium carbonate until the salt is completely dissolved and the precipitated silver carbonate has again passed entirely into solution. The mixture is slowly poured into methyl alcohol which has been freshly distilled over lime, after which it is allowed to remain at rest for about twenty-four hours until the precipitate has completely subsided. The supernatant liquid should now be colourless. The precipitate is carefully washed with alcohol by decantation and finally on the filter. The filtrate and washings are united, freed from alcohol by evaporation on the water-bath, cooled, acidified with nitric acid, and titrated according to Volhard's method. H. W.

**The Preparation of Lead Test-papers and Notes on the Titration of Zinc with Sodium Sulphide.** E. OLIVIER (*Bull. Soc. chim. Belg.*, 1922, **31**, 102—109).—Experimental details of the method used in the author's laboratory for titrating zinc solutions are described and instructions for making and testing the lead papers used as indicators given. The presence of free ammonia owing to its solvent action on zinc sulphide, introduces an error the substance should be removed by boiling or by neutralisation. Further, ammonium salts should not be present in excess, otherwise the clearness of the end-point is impaired. H. J. E.

**Estimation of Zinc as Sulphate.** A. GUTBIER and K. STAI (*Z. anal. Chem.*, 1922, **61**, 97—103).—Zinc salts may be converted into sulphate by evaporation with sulphuric acid in a platinum basin, heating the residue at about 500° for fifteen minutes, cooling it, adding a small quantity of water, and repeating the evaporation and heating; the residue then consists of anhydrous zinc sulphate and may be weighed as such; zinc sulphate does not dissociate below 675°. If desired, the sulphate may be heated over a blast-flame until no further loss in weight occurs, and the resulting zinc oxide weighed. W. P. S.

**Rapid Analysis of White Metal and Similar Alloys.** L. ·IAUX (*Ann. Chim. Analyt.*, 1922, **4**, 77—79).—Antimony is

estimated in one portion by solution of the sample in sulphuric acid followed by titration with permanganate. A second portion of 10 grams is mixed with fine tin filings equal to ten times the antimony content of the alloy and the mixture is treated with sufficient nitric acid to dissolve everything. The resulting mass is boiled with a large quantity of water to precipitate completely the tin and antimony, the liquid is cooled, made up to bulk, and an aliquot part filtered through a dry paper and used for the estimation of the other metals by any convenient process. The tin is determined by difference. [Cf. *J. Soc. Chem. Ind.*, 1922.]

A. R. P.

**Estimation of Aluminium in Tungsten.** VICTOR FROBOESE and KÄTHE FROBOESE (*Z. anal. Chem.*, 1922, **61**, 107—110).—About 3 grams of the finely divided metal are ignited in a platinum crucible for one hour, then fused with the addition of a mixture of potassium carbonate and sodium carbonate, and cooled; the mass is dissolved in water, and the solution filtered. The filtrate, which may contain a trace of aluminium, is evaporated nearly to dryness, acidified with hydrochloric acid, evaporated, the dry residue treated with dilute hydrochloric acid and water, and the solution filtered; this filtrate is boiled, rendered alkaline with sodium hydroxide, again acidified, the aluminium is precipitated as hydroxide by the addition of ammonia, and the precipitate is collected, ignited, and weighed. The main quantity of the aluminium remains in the insoluble portion from the carbonate fusion; this insoluble portion is ignited in a platinum crucible, heated with hydrofluoric acid and a drop of sulphuric acid, fused with potassium pyrosulphate, the mass dissolved in water and sulphuric acid, and the solution filtered. The filtrate is treated with "cupferron" reagent to precipitate the iron, and the aluminium is then precipitated in the usual way in the filtrate from the iron precipitate. W. P. S.

**Estimation of Free Acid in Acid Aluminium Sulphate Solutions.** H. ZSCHOKKE and L. HÄUSELMANN (*Chem. Ztg.*, 1922, **46**, 302).—The following modification of Ivanov's method (A., 1913, ii, **343**, 1078) is recommended. Ten c.c. of the aluminium sulphate solution, 10 c.c. of barium chloride solution (1 : 10), 5 c.c. of potassium ferrocyanide solution (1 : 10) which must not be more than six days old, and 60 c.c. of boiling water are poured in the above order into a 100 c.c. flask. A gelatin solution (1 : 50) is added drop by drop with agitation until the precipitate that is formed becomes flocculent and settles easily. The mixture is cooled and diluted to 100 c.c., allowed to settle, and filtered. Fifty c.c. of the clear, colourless filtrate are diluted with 50 c.c. of water and titrated with $N/10$-sodium hydroxide until neutral to methyl-orange. The temperature of the solution must never exceed 85°, and the excess of potassium ferrocyanide must not be too great, or low results will be obtained. If the quantity of acid present be more than 6 grams per litre, the filtrate remains cloudy, when a few drops of $N/10$-sodium hydroxide should be added before precipitation. H. C. R.

**Estimation of Manganese as Sulphate.** J. HUBER (*Z. ana Chem.*, 1922, **61**, 103—107).—Manganese sulphate is rendere anhydrous by heating it at 360—400°; dissociation commence only at 650°. W. P. S.

**Estimation of Manganese by Permanganate and Investigation of some Manganites.** P. B. SARKAR and N. R. DHAI (*Z. anorg. Chem.*, 1922, **121**, 135—155).—The authors find tha manganese can be accurately estimated by permanganate if on of the following salts is present: magnesium sulphate, potassiun nitrate, potassium sulphate, cadmium sulphate, sodium nitrate potassium fluoride, sodium acetate and lithium, sodium, calcium barium, and strontium chlorides. Some of the metals of thes salts form manganites, others simply coagulate the hydrate manganese dioxide formed and thus make possible a sharp end point. Coloured salts cannot be used, neither did the titration succeed in the presence of such sparingly soluble salts as calciun phosphate or sulphate, etc., because the concentration of electrolyte is too small. The preparation, composition, and propertie of several manganites are described, and the formation of manganite and the position of the metal in the periodic system discussed Absolutely pure hydrated manganese dioxide can be prepare by heating a solution of manganous sulphate and sodium nitrat and gradually adding potassium permanganate to the well-stirre mixture. The precipitate is filtered and well washed with ho water. W. T.

**The Estimation of Manganese by Knorre's Persulphate Method.** P. NICOLARDOT, M. GELOSO, and E. RÉGLADE (*Ann Chim. Analyt.*, 1922, **4**, 69—77, 102—110).—Manganese dioxide precipitated from sulphate solutions by boiling with ammonium persulphate, contains less than the theoretical amount of oxygen unless at least nine times as much iron is present, and if the precipitate is dissolved in ferrous sulphate solution and the excess of the latter titrated with permanganate, the manganese factor of the permanganate varies from 0·498 × iron factor with pure solutions of manganese sulphate to 0·49176 × iron factor when the original solution contains a large excess of iron. Variations in the acidity of the solution have very little effect, especially in the presence of iron, as long as the free acid does not exceed 5%; in any case, traces of manganese remain in the mother-liquor and should be estimated by boiling the solution with a further quantity of persulphate and a little silver nitrate and titrating the permanganate so formed with standard sodium arsenite. Of the common metals likely to be present in the solution, cobalt gives very, and nickel slightly, high results. Instructions are given for estimating manganese in ferromanganese and spiegeleisen. [Cf. *Soc. Chem. Ind.*, 1922, May.] A. R. P.

**Titration of Tin with Ferric Chloride.** L. SMITH (*Z. anal. Chem.*, 1922, **61**, 113—120).—The hydrochloric acid solution of salt is boiled, pieces of zinc foil are added, and, after about

ten minutes, the mixture is again boiled, and a further quantity of zinc is added, followed by hydrochloric acid. When all the metal is in solution, hot water is added slowly so that the boiling is not interrupted, and the solution is then titrated with ferric chloride solution. The end-point of the titration is denoted by the appearance of a greenish-yellow coloration. About 5 grams of zinc are required for each gram of tin to be reduced, aud zinc is preferable to aluminium for the purpose. W. P. S.

**Micro-analysis of Organic Substances.** G. WELTER (*Ann. Chim. Analyt.*, 1922, **4**, 33—37).—Micro-chemical methods may be used for the estimation of carbon, hydrogen, nitrogen, halogens, sulphur, methoxyl groups, phosphorus, etc., in organic substances; these methods are described briefly. Only a few mg. of the substance are required for an estimation, but all weighings must be made on a balance sensitive to 0·001 mg. The error in the results obtained is about 0·5%. W. P. S.

**The Estimation of Aromatic Hydrocarbons in Mineral Oil Fractions.** H. I. WATERMAN and J. N. J. PERQUIN (*Rec. trav. chim.*, 1922, **41**, 192—198).—An attempt to apply the " aniline point " method of Tizard and Marshall (A., 1921, ii, 280) to the estimation of aromatic hydrocarbons in various mineral oils and their products shows that the nature of the fraction influences the result considerably. Experiments carried out with oils containing added benzene, naphthalene, and phenanthrene show that addition of equal weights of these substances does not produce equal effects on the " aniline point." H. J. E.

**Estimation of Glycerol by the Dichromate Method.** J. KELLNER (*Z. deut. Oel-Fett-Ind.*, 1921, **14**, 751—752; cf. Steinfels, *Seifensieder Ztg.*, 1915, **42**, 721; Tortelli and Ceccherelli, A., 1914, ii, 750).—Analysis of glycerol by Steinfels's (*loc. cit.*) dichromate method gives low results unless sulphuric acid, *d* 1·230, is used instead of that of *d* 1·175. CHEMICAL ABSTRACTS.

**Physiology of the Phenols. I. The Estimation of Phenols in the Blood.** K. F. PELKAN (*J. Biol. Chem.*, 1922, **50**, 491—497).—The method of Folin and Denis (A., 1912, ii, 1011) is modified and made applicable to blood. No heat is used in the precipitation of proteins and the concentration of filtrates, since this would cause a loss of volatile phenols. The estimation is performed on 10 c.c. of blood. Proteins are removed by shaking with tungstic acid and alumina cream, and the uric acid is precipitated by the addition of a solution of silver lactate in lactic acid. Free phenols are then estimated colorimetrically in one portion of the filtrate, using a phosphotungstic–phosphomolybdic reagent, whilst in a second portion the estimation is performed after heating for ten minutes on a water-bath with a few drops of concentrated hydrochloric acid. If the last operation is carried out in a narrow tube no loss of volatile phenols occurs and the difference between the two results then represents conjugated phenols. Since lactic acid gives a coloration with the phosphotungstic–phosphomolybdic

reagent, the standard must be treated with a corresponding amount of the silver lactate reagent (cf. Benedict and Theis, A., 1918, ii, 461). E. S.

**Detection of β-Naphthol in Foods, Spices, and Beverages.** YUTAKA KINUGASA and HISAJIRÔ TATSUNO (*J. Pharm. Soc. Japan*, 1922, 18—24).—The method is based on Riegler's method for the detection of nitrous acid (A., 1897, ii, 464). When a solution (1 c.c.) suspected to contain β-naphthol is treated with 2 drops of 0·1% sodium 1 : 4-naphthylaminesulphonate solution, 1 drop of 0·1% nitrous acid, and 1 drop of hydrochloric acid, shaken, and ammonia added, a red coloration is produced. The colour occurs with 1/1000 mg. of β-naphthol per litre. Colorations are also given by this reagent with the following substances in concentration of 1/100,000: α-naphthol, violet-red; resorcinol, quinol, phloroglucinol, pyrogallol and thymol, all yellow; phenol, orange-red; benzoic and cinnamic acids, almost colourless, and salicylic acid, slight yellow. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] K. K.

**Distillation Method for the Estimation of Santalol in Santal Oil.** C. W. HARRISON (*J. Assoc. off. Agric. Chem.*, 1921, **5**, 166—171).—In the U.S. Pharmacopœia method for estimating santalol in santal oil, the latter is acetylated and a known quantity of the dry product saponified. From the amount of alkali required to saponify the oil, the percentage of santalol present in the original substance is calculated by means of a formula given. When the santal oil is adulterated with a saponifiable oil, the method is not applicable. A modified method, which, however, is not yet completely standardised, is suggested. It consists in acidifying the product obtained after the saponification of the acetylated oil, distilling in a current of steam under specified conditions, and estimating by titration the acidity of the distillate. From this figure the percentage of santalol in the original oil can be calculated. [Cf. *J. Soc. Chem. Ind.*, 1922, 346A.] J. R.

**The Estimation of Small Quantities of Dextrose by Bertrand's Process.** IRENE GREINER (*Biochem. Z.*, 1922, **128**, 274—278).—Accurate results for the estimation of quantities of dextrose less than 10 mg. are obtained by Bertrand's process, if 10 c.c. of the sugar solution are taken, mixed with 10 c.c. of the copper sulphate solution and 10 c.c. of a solution containing 150 grams of sodium carbonate and 30 grams of sodium hydrogen carbonate per litre are added, followed by 10 c.c. of the sodium potassium tartrate solution, and the process carried out in the standard manner, except that, after boiling the solution for three minutes, it is allowed to cool for fifteen minutes. For the titration the use of a 5 c.c. burette graduated in 1/50 or 1/100 c.c. is recommended. A table showing mg. of copper equivalent to 1 to 10 mg. of dextrose is given. H. K.

**A Colorimetric Method for the Estimation of Sugars in Normal Human Urine.** OTTO FOLIN and HILDING BERGLUND (*J. Biol. Chem.*, 1922, **51**, 209—211).—Reducing substances are

removed from the urine by treatment with "Lloyd's alkaloidal reagent," which is described as a concentrated fullers' earth. The sugars are then estimated in the filtrate by the method of Folin and Wu (A., 1920, ii, 337). For total sugar, a separate portion of the filtrate is first hydrolysed by boiling with hydrochloric acid.

E. S.

**Inhibition Phenomena in Amylases.** URBAN OLSSON (*Z. physiol. Chem.*, 1922, **119**, 1—3; cf. this vol., i, 390).—A method for measuring the liquefaction of starch is based on the principle of recording the time taken by a glass ball to drop in the starch solution contained in an evacuated tube. S. S. Z.

**The Estimation of Pectin as Calcium Pectate and the Application of this Method to the Estimation of the Soluble Pectin in Apples.** MARJORY HARRIOTTE CARRÉ and DOROTHY HAYNES (*Biochem. J.*, 1922, **16**, 60—69).—Pectin can be estimated as calcium pectate, empirical formula $C_{17}H_{22}O_{16}Ca$, by precipitation with calcium chloride and hydrochloric acid under determined conditions. A method is described for the extraction of the soluble pectin from apples, and some analytical results are given. W. O. K.

**A Reaction of Wood and some Observations on Anethole.** OSKAR ADLER (*Biochem. Z.*, 1922, **128**, 32—34).—All varieties of wood when warmed with a glacial acetic acid solution of phenylhydrazine hydrochloride become coloured green, adhering fragments of bark becoming reddish-brown. The colours fade on prolonged warming. Furfuraldehyde (but not pentoses), oil of anise, and oil of fennel give this green coloration. Anethole is a constituent of these oils and gives the coloration when of commercial purity, but when pure does not. The constituent responsible for the reaction has not been traced, but it distils over with anethole and is produced from anethole by oxidising agents, by the action of ultra-violet light, and by prolonged heating. Known oxidation products of anethole and allied substances do not give the reaction. H. K.

**The Analysis of Partly Hydrolysed Fats. II.** W. FAHRION (*Chem. Umschau*, 1922, **29**, 54—55, 60—61, 66—67, 75—76, 88—89).—In using the factor (100 × acid number)/(saponification number) for calculating the percentage of free fatty acids in a sample of partly hydrolysed fat, it is assumed (1) that the saponification value of the neutral fat is the same as the acid value of the fatty acids obtained from it, and (2) that the free fatty acids have no ester value, their acid value being the same as their saponification value. Neither of these assumptions is justified. The former assumption overlooks the fact that the weight of fatty acids obtained is only about 95% of the weight of fat treated, and involves an error in the percentage of free fatty acids amounting to a maximum of +1·1% when there are 50% present. That the latter assumption is not justified is shown by a list of acid values and saponification values of the fatty acids of various oils and fats. In almost every

case the saponification value is higher than the acid value, the difference being more than 10 units in the case of the fatty acids from cotton seed, apricot kernel, cherry kernel, walnut and linseed oils, and palmitic and oleic acids, especially when the oils or fatty acids have been stored for long periods in the light. This difference is shown to an even greater degree by the fatty acids of kapok and baobab oils and by those of certain marine oils. It has been explained by supposing a linking up of carbonyl groups with ethylenic linkings, but the case of palmitic acid cannot be explained in this way. A third assumption made in using the above formula is that the various glycerides in a fat are all split at the same rate. This is approximately true in the case of alkaline saponification, but it is doubtful if this is so in that of hydrolysis with steam, castor seed lipase, or hydrochloric acid. For example, castor seed lipase scarcely attacks triacetin and hydrolyses tributyrin incompletely, and the neutral fat from a sample of palm kernel oil partly hydrolysed by steam under pressure showed a markedly lower saponification number than the free fatty acids. Therefore the quantity of free fatty acids in partly hydrolysed fats cannot be calculated from the acid number, because the acid number of the fatty acids can appreciably fall both during the process and afterwards.

H. C. R.

**The Analysis of Sour Milk.** André Kling and Arnold Lassieur (*Ann. Falsif.*, 1922, **15**, 95—101).—If the state of the milk is such that the sample cannot be made homogeneous, the estimation must be carried out on the whole sample. The "extract at 100°" of a milk no longer fresh must always be suspect, and may be very different from that of the fresh milk. It bears no relation to the appearance of the sample when analysed. The estimation of butter fat is more trustworthy, and varies little with time. The acidity of the fat obtained should, however, be determined to ensure that the glycerides are not partly hydrolysed. The estimation of casein precipitated by acetic acid is quite untrustworthy in the case of sour samples. The estimation of lactose is of doubtful value, but is best done by Hildt's method. The ash is affected by the partial volatilisation of chlorides to the extent of about 2%. The total nitrogen is quite unaffected. It is therefore recommended that decisions on samples of milk which have become sour should be based on estimations of butter fat and total nitrogen.

H. C. R.

**A Rapid Method for the Estimation of Acetaldehyde.** N. K. Smitt (*Bull. Bur. Bio-Tech.*, 1922, No. 5, 117—118).—Benzidine hydrochloride gives a yellow coloration with acetaldehyde, which increases in intensity with time and finally becomes brown or orange. Formaldehyde gives a similar colour with the reagent, but in this case it develops only slowly. For the estimation of acetaldehyde in solution, the solution is diluted until it contains from 0·1 to 5% and then to 5 c.c. of the diluted solution 5 c.c. of the benzidine hydrochloride solution are added and after thirty

minutes the colour is matched against a set of standard tubes of acetaldehyde to which the reagent was added at the same time. The method is not, however, sufficiently sensitive to be used for the estimation of very small amounts of acetaldehyde. W. G.

**Detection of Acetaldehyde in Urine.** WILHELM STEPP (*Biochem. Z.*, 1922, **127**, 13—17).—Five % of a diluted urine is distilled through a fractionating column and the vapour absorbed in ice-cold water. The presence of acetaldehyde is best recognised by combination with dimethylhydroresorcinol. H. K.

**[Estimation of] Vanillin.** E. TSCHIRSCH (*Seifensieder Ztg.*, 1921, **48**, 856).—Two grams of vanillin (m. p. 80—81°) are mixed with 100 c.c. of water and 30 c.c. of *N*/2-potassium hydroxide solution, the mixture being kept cold, and frequently shaken, for two hours; it is then titrated with *N*/2-sulphuric acid. The difference multiplied by 3·8 gives the percentage of vanillin.
CHEMICAL ABSTRACTS.

**Estimation of Digitoxin in Digitan.** L. E. WARREN (*J. Amer. Pharm. Assoc.*, 1922, **11**, 8—12).—No satisfactory method of estimating digitoxin has been described, but the Keller method as modified by Fromme is considered the best. Digitan is a mixture of the tannates of the glucosides of digitalis diluted with lactose. The Keller method modified by omitting clarification with lead acetate yielded a digitoxin fraction which, when tested pharmacologically, had only about 17% of the activity of pure digitoxin.
CHEMICAL ABSTRACTS.

**The Hypobromite Reaction on Urea.** PAUL MENAUL (*J. Biol. Chem.*, 1922, **51**, 87—88).—The author was unable to obtain accurate results in the estimation of urea by Stehle's modification (A., 1921, ii, 605) of the hypobromite method.
E. S.

**The Gasometric Estimation of Urea.** RAYMOND L. STEHLE (*J. Biol. Chem.*, 1922, **51**, 89—92).—A reply to Menaul (cf. preceding abstract). E. S.

**The Electrometric Estimation of Cyanides in the Presence of Haloids.** ERICH MÜLLER and HANS LAUTERBACH (*Z. anorg. Chem.*, 1922, **121**, 178—192).—The electrometric estimation of cyanides was carried out by Treadwell (A., 1911, ii, 827). When silver nitrate solution is run into a solution of a cyanide containing a silver electrode a sudden increase of potential is observed when CN : Ag=2 : 1 corresponding with the completion of the reaction $2CN'+Ag^{\cdot}=Ag(CN)_2'$ (1). This sudden change is due to the commencement of the reaction $Ag(CN)'_2+Ag^{\cdot}=2AgCN$ (2). The authors found another sharp change in the potential when reaction (2) is completed and the concentration of silver-ion in the solution increases. This second maximum rate of change of potential is more accurate than the first, which gives a slightly low result. This second point is also of importance in the estimation of a

mixture of cyanide and haloids. The solubility products of th silver salts are $AgI = 10^{-16}$; $AgBr = 6{\cdot}4 \times 10^{-13}$; $AgCN = 4{\cdot}8 \times 10^{-12}$ $AgCl = 10^{-10}$. Saturated solutions of these salts contain a higher con centration of silver ion than a solution of potassium silver cyanide because they are all soluble in a solution of potassium cyanide Hence a solution containing cyanide and haloids should give severa sharp changes of potential in an electrometric titration whicl would correspond with the end of the several precipitations. Th solubilities of the bromide, cyanide, and chloride of silver ar near to one another and sudden changes of potential correspondin with these three were not observed.

The results obtained were as follows :

| | | |
|---|---|---|
| (I+CN) | three sudden changes giving | (1) $\frac{1}{2}$CN (2) $\frac{1}{2}$CN+I (3) CN+(I) |
| (Br+CN) | two ,, ,, ,, | (1) $\frac{1}{2}$CN (2) CN+Br |
| (Cl+CN) | ,, ,, ,, ,, | (1) $\frac{1}{2}$CN (2) CN+Cl |
| (I+Br(or Cl)+CN) | three ,, ,, | (1) $\frac{1}{2}$CN (2) $\frac{1}{2}$CN+I (3) CN+I+Br(or Cl) |
| (Br+Cl+CN) | two ,, ,, | (1) $\frac{1}{2}$CN (2) CN+Br+Cl |

The apparatus is described. W. T.

**Sensitiveness of certain Tests for Hydrocyanic Acid.** THURE SUNDBERG (*Z. anal. Chem.*, 1922, **61**, 110—112).—The author agrees with the statement of Kolthoff (A., 1918, ii, 128) that the ferrocyanide reaction is the most trustworthy for the identification of hydrocyanic acid; the test will detect as little as 0·023 mg. of hydrogen cyanide in 10 c.c. of solution. Other sensitive tests are the guaiacum–copper sulphate test (0·001 mg. HCN) and the copper–benzidine acetate test (0·005 mg. HCN; A., 1921, ii, 224). W. P. S.

**Modification in the Process of Extraction of Alkaloids.** DOMENICO LIOTTA (*Arch. Farm. sperim. Sci. aff.*, 1921, **32**, 27—30; cf. A., 1920, i, 587).—The estimation of nicotine in tobacco may be simplified as follows. The dried, powdered material (1·5—3 grams) is completely decolorised by treatment with chlorine and then steeped in water at the ordinary temperature for twenty-four to forty-eight hours. From the resulting solution the nicotine is precipitated by means of silicotungstic acid, the precipitate being calcined; multiplication of the weight of the calcined residue by 0·1139 gives the weight of nicotine present in the sample taken. The method gives results in good agreement with those furnished by the ordinary method, and is doubtless applicable to the estimation of other alkaloids. T. H. P.

**Estimation of the Alkaloids in Extract of Aconite.** A. ASTRUC, E. CANALS, and R. BORDIER (*J. Pharm. Chim.*, 1922, **25**, 161—164).—The official method of the French Codex for the estimation of the alkaloids in extract of aconite gives low results owing to their incomplete extraction by the specified quantity of ether. The following method of operation is recommended in preference: 5 grams of extract are diluted to 25 c.c. with water, 10 c.c. of 10% nitric acid are added, followed by 5 c.c. of ammonia, and the solution is extracted three times with quantities of 100 c.c. of ether with vigorous and repeated agitation during ten minutes

for each extraction. It is then extracted four times with 50 c.c. of ether, and the fourth extract should be free from alkaloid when tested with Valser and Mayer's reagent. The alkaloids in the united ethereal extracts are then transferred to aqueous solution by shaking with dilute nitric acid followed by four washings with water, and they are then precipitated in the usual way from the filtered aqueous solution by adding 15 c.c. of 5% silicotungstic acid and 20 c.c. of 10% nitric acid. The precipitate is collected on a filter and ignited, and the weight of the residue multiplied by the factor 0·793 gives the weight of alkaloid in the 5 c.c. of extract taken. G. F. M.

**Method for the Estimation of Procaine [Novocaine].** A. W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1921, 5, 163—166).—When novocaine is heated with 0·1*N*-sodium hydroxide solution, it is hydrolysed with a quantitative formation of sodium *p*-aminobenzoate. This compound without extraction can be titrated with a mixed potassium bromide and potassium bromate reagent under specified conditions. The estimation depends on the fact that each molecule of novocaine reacts with 3 molecules (6 atoms) of bromine. [Cf. *J. Soc. Chem. Ind.*, 1922, 345A.] J. R.

**The Estimation of the Purine Bases in Urine.** E. SALKOWSKI (*Z. physiol. Chem.*, 1922, **119**, 121—124).—Estimations of the purine bases carried out by Fridericia showed that the silver method of the author gives lower results than the Krüger-Schmid method. This is interesting in view of Steudel and Chon's recent results (this vol., ii, 239). S. S. Z.

**Estimation of Uric Acid in Blood.** A. GRIGAUT (*Bull. Soc. Chim. Biol.*, 1922, **4**, 11—22).—Proteins are precipitated by metaphosphoric acid and the colorimetric method of Folin and Denis (A., 1913, ii, 162) is then applied directly to the protein-free filtrate. E. S.

**Estimation of Uric Acid in Blood.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **51**, 187—207).—In the colorimetric method described, a new arsenic phosphotungstic acid reagent is used which, with uric acid, produces a much greater depth of colour than the phosphotungstic acid reagent. The new reagent is prepared by adding 50 grams of arsenic pentoxide, 25 c.c. of 85% phosphoric acid, and 20 c.c. of concentrated hydrochloric acid to a solution of 100 grams of sodium tungstate in 600 c.c. of water, boiling for twenty minutes, and finally diluting to 1 litre. For the estimation, proteins are removed from the blood by the tungstic acid method and 5 c.c. of the filtrate are taken. After dilution to 10 c.c., 4 c.c. of a 5% sodium cyanide solution containing 2 c.c. of concentrated ammonia per litre and 1 c.c. of the arsenic phosphotungstic acid reagent are added and the mixture is immersed in boiling water for three minutes. After cooling, the colour developed is compared with a standard. Results obtained by this method are usually somewhat higher than those obtained by the precipitation method of Folin and Wu (A., 1919

ii, 308). The possible causes of this and the relative merits of the two methods are discussed at some length in the original.
E. S.

**A New Colorimetric Method for the Estimation of Plasma Proteins.** HSIEN WU (*J. Biol. Chem.*, 1922, **51**, 33—39).—The method depends on the colour reaction which the three proteins give with phospho-18-molybdotungstic acid (phenol reagent) in the presence of sodium carbonate. A tyrosine standard is used, estimations by the Kjeldahl method having shown that, for human plasma, 1 mg. of tyrosine is equivalent to 16·4 mg. of fibrin, 25·2 mg. of globulin, or 27·5 mg. of albumin. Separation of the proteins is effected, in the main, by the method of Cullen and Van Slyke (A., 1920, ii, 398). Fibrin and albumin, after purification, are estimated directly, whilst the albumin and globulin contained in the filtrate from the fibrin are precipitated and estimated together. The value for the globulin is then obtained by difference. E. S.

**The Tyrosine Content of Proteins.** OTTO FÜRTH and WALTER FLEISCHMANN (*Biochem. Z.*, 1922, **127**, 137—149).—A comparison of the various processes for the estimation of tyrosine in proteins shows that the quantity of tyrosine which can be isolated gravimetrically is far below that estimated. The method of Folin and Denis (A., 1912, ii, 1012), and the colorimetric estimation by the diazo-reaction and by Millon's reagent give maximum values, the most suitable method being the absorption of bromine in acid solution by the protein hydrolysate after removal of substances precipitable by phosphotungstic acid. H. K.

**Micro-estimation of Albumin.** C. VALLÉE and M. POLONOWSKI (*Compt. rend. Soc. Biol.*, 1921, **84**, 901—903; from *Chem. Zentr.*, 1921, iv, 1080).—The total nitrogen is estimated in 1 c.c. of the liquid under examination by the method previously described (this vol., ii, 312). In a further 2—3 c.c. of the liquid the albumin is precipitated by addition of two drops of glacial acetic acid and a small quantity of sodium chloride, and heating on a water-bath at 90°. The liquid is made up to the original volume, centrifuged, and the nitrogen estimated in an aliquot portion of the clear liquid. The albumin nitrogen is thus obtained by difference. G. W. R.

**Estimation of Pepsin.** H. W. VALTEICH and C. C. GLOVER (*J. Amer. Pharm. Assoc.*, 1921, **10**, 595—606).—Comparative examination of methods for the estimation of pepsin showed that whilst Northrup's electrolytic method is trustworthy, the best method is that of U.S.P. IX, although the use of storage eggs instead of fresh eggs is recommended. CHEMICAL ABSTRACTS.

**A New Method for the Estimation of Pepsin.** KARL GLÄSSNER (*Biochem. Z.*, 1922, **127**, 312—315).—This method is a precipitation method and depends on the observation that globin (readily prepared from hæmoglobin by a slight modification of Strauss and Grützner's method; A., 1921, i, 200) is precipitated from hydrochloric acid solution by ammonia and is insoluble in

excess of ammonia, especially if a few drops of ammonium chloride are added. A series of dilutions of pepsin or gastric juice and acid in geometrical progression are made and 1% globin solution is added to each. After digestion at 40° for fifteen minutes, addition of 3—5 drops of ammonium chloride solution (10%) and 1—2 c.c. of 1% ammonia solution gives a flocculent precipitate in the tubes containing undigested globin. H. K.

**Tannase.** DONALD RHIND and FRANCIS EDWARD SMITH (*Biochem. J.*, 1922, **16**, 1—2).—A method has been elaborated for estimating the hydrolysing power of tannase by measuring the tannin present in a solution before and after action by the enzyme for varying periods. The tannin is estimated by titrating the whole solution with potassium permanganate in presence of indigo-carmine, the tannin is then removed by Nierenstein's caseinogen method (A., 1911, ii, 236), and the solution is again titrated with potassium permanganate. The difference between the two titrations represents the amount of gallotannin present. W. O. K.

**Estimation of Peroxydase in Milk.** FRANCIS E. RICE and TORATORO HANZAWA (*J. Ind. Eng. Chem.*, 1922, **14**, 201—202).—The method of Bach and Chodat for the estimation of peroxydase in plant juices (A., 1904, i, 542) is adapted for milk. It depends on the oxidation of pyrogallol by hydrogen peroxide, the reaction being catalysed by peroxydase. The number of mg. of purpurogallin precipitated by the action of 10 c.c. of milk is called the "peroxydase number." The reaction takes seven days, and air must be excluded. The residue after filtration is washed with light petroleum to remove fat. Whole and skim milk are about equal in peroxydase activity. Heating milk below 68·3° for thirty minutes reduces, but does not destroy peroxydase activity, which is also reduced slightly by keeping on ice for two days. Samples of milk for the estimation of peroxydase cannot be preserved with mercuric chloride or formaldehyde. H. C. R.

**Estimation of the Antiscorbutic Vitamin (Vitamin-*C*).** H. C. SHERMAN, V. K. LAMER, and H. L. CAMPBELL (*J. Amer. Chem. Soc.*, 1922, **44**, 165—172).—A modified diet free from vitamin-*C* and containing an adequate amount of vitamin-*A*, namely, ground oats 59%, skim milk powder, heated on open trays at 110°, 30%, freshly prepared butter fat 10%, and sodium chloride 1% is recommended. The method of measurement consists in a series of observations on animals receiving no vitamin-*C* and different measured amounts up to the amount which affords complete protection, and permits optimum growth. The symptoms and autopsy findings are interpreted in terms of the percentage of the required amount of antiscorbutic vitamin which was actually received by the animal in any individual case. W. G.

**Blood Analysis. IV. Ashing Methods.** M. RICHTER-QUITTNER (*Biochem. Z.*, 1921, **126**, 97—104).—For the estimation of total alkali metals, phosphorus and iron, for example, in blood,

ashing methods can be employed successfully. Corpuscles contair fewer mineral constituents than serum and still less if the flow oi blood be stemmed in a vein. H. K.

**Analysis of Blood and Urine. I.** LUDWIG PINCUSSEN and ARISTOMENIS FLOROS (*Biochem. Z.*, 1921, **125**, 42—45).—To avoid the expensive torsion balance in Bang's micro-methods, the authors recommend a fine graduated pipette holding 0·1 gram of blood. By working quickly the same pipette can be used for measuring the two drops of blood, for duplicate analysis, without use of an anti-clotting agent. Examples are given of the estimation of the reducing sugar of blood. Bang's method foı the analysis of sugar in blood is applicable to sugar in urine if the coagulable protein is removed by addition of 12 c.c. of 0·05% copper sulphate solution to 1 c.c. of diluted urine (1 : 100). The results agree with the macro-method. Other substances which produce a high reduction figure are creatine and uric acid, the urine of persons with an increased uric acid and creatine content showing increased reduction. H. K.

**Analysis of Blood and Urine. II.** LUDWIG PINCUSSEN and KATE MOMFERRATOS-FLOROS (*Biochem. Z.*, 1921, **125**, 46—48).—For the micro-estimation of acetone in urine, a brisk current of air is drawn for twenty-five minutes through 1—2 c.c. of urine, mixed with 20—30 mg. of oxalic acid, 0·5 gram of sodium chloride and 5 c.c. of water, and the free acetone absorbed by 10—15 c.c. *N*/100-iodine solution mixed with 1 c.c. of 33% sodium hydroxide solution. The excess of iodine is estimated volumetrically after acidifying. The combined acetone as acetoacetic acid is obtained by changing the receiver and passing the current of air through the boiling solution. For the estimation of ammonia in blood, 5 c.c. mixed with 0·2% potassium oxalate were treated with 0·1 c.c. of sodium hydroxide solution and the volume made up to 25 c.c. exactly with alcohol, whereby protein is precipitated. The solution is filtered rapidly into a vessel containing a drop of dilute acid to fix the ammonia. Twenty c.c. of filtrate were made alkaline with sodium carbonate solution and a current of air was passed through for fifteen minutes at 40° and the ammonia absorbed by 2 c.c. of *N*/50-sulphuric acid. H. K.

**Method for the Estimation of Total Base in Urine.** CYRUS H. FISKE (*J. Biol. Chem.*, 1922, **51**, 55—61).—Organic matter is removed from the urine by evaporation with a mixture of sulphuric and nitric acids. Phosphates are removed from the residue by the ferric chloride–ammonium acetate method, after which the filtrate is evaporated to dryness and ignited first with sulphuric acid and then with ammonium carbonate. The residue contains the sulphates of sodium, potassium, calcium, and magnesium. Estimation of sulphate by the benzidine method (A., 1921, ii, 556) gives the equivalent of the bases present. E. S.

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# General and Physical Chemistry.

**The Rôle of the Physicist in the Development of Chemical Theory.** Presidential Address. Delivered at the Annual General Meeting, March 30th, 1922. SIR JAMES WALKER (T., 1922, **121**, 735—745).

**Relationships between Molecular Refraction and Other Properties.** W. HERZ (*Z. physikal. Chem.*, 1922, **101**, 54—62).—From Berthelot's equation, $M=11\cdot4\,d\,\{T_k/p_k(2-T/T_k)\}$ (A., 1899, ii, 404), and Guye's expression, $MR=1\cdot8T_k/p_k$, in which $MR$ is the molecular refraction and the other symbols have their usual significance, the author has derived the expression $M/d_s=5MR$, where $d_s$ is the density at the boiling point. This expression says that the molecular volume for non-associated liquids at the boiling point has a value equal to five times the molecular refraction. This statement has been tested for thirty-three substances and shown to be fairly in keeping with facts in the case of the simpler aliphatic liquids, but in the case of halogen-substituted compounds, aromatic, heterocyclic, and inorganic substances, large divergences are observed. The expression $MR=M/5d_s=0\cdot9c/d_kT_s$ is deduced, from which $M=11\cdot97c/T_s$ is obtained, where $c$ is the molecular boiling-point elevation constant. This equation is shown to be in keeping with fact to the extent of 10—20%. Further expressions are derived by which from the molecular volume at the boiling point and the molecular refraction the molecular diameter and the internal pressure may be calculated. In many cases it is shown that $ML/MR=8p_k$, where $L$ is the latent heat of vaporisation at the boiling point. A constant relationship is shown to exist between the coefficient of expansion, the molecular refraction, and the critical pressure, which has the form $MRp_k/(1/k_{20}+293)=$ constant (0·9). Evaluation of this constant for seventeen substances gives figures which lie between the extremes 1·38 and 0·84.

J. F. S.

**Regularities in Systems of Bands.** A. KRATZER (*Ann. Physik*, 1922, [iv], **67**, 127—153).—The work of Heurlinger (*Diss. Lund.*, 1918), and Lenz (*Verh. Deut. physikal. Ges.*, 1919, **21**, 632) on series lines in band spectra is extended by the application of the quantum theory to the consideration of the anharmonic vibrations of a molecular oscillator. A formula, similar to that deduced empirically hy Deslandres (A., 1920, ii, 69) is obtained for the zero lines in a series of bands, and is found to represent very exactly the lines in the band spectrum of oxygen and the lines in the violet band spectrum of cyanogen. The significance of the constants in Deslandres's formula is interpreted on tbe basis of the quantum theory, and a formula involving nine constants is obtained, to represent the whole of the lines in the violet band spectrum of

cyanogen, exclusive of the fine structure. The application of the theory to the lines in the red band spectrum of cyanogen and the band spectrum of nitrogen is briefly indicated. J. S. G. T.

**The Structure of the Balmer Series.** OTTO OLDENBERG (*Ann. Physik.*, 1922, **67**, 69—72).—The new measurements of McLennan and Lowe (A., 1921, ii, 666) for the $H_\alpha$, $H_\beta$, $H_\gamma$, and $H_\delta$ lines are not considered to be in opposition to the Sommerfeld theory of the structure of the Balmer series, the differences being explained by the neglect of the small shift which is caused by the steep rise in intensity of a neighbouring line. Experiments with the discharge tube used by Wood (A., 1920, ii, 569) indicate that the third members of the triplets found by McLennan and Lowe are not produced in the absence of nitrogen. The new lines which are observed on the admission of nitrogen are found to be somewhat sharper than the Balmer doublet. W. E. G.

**Extension of the *X*-Ray Spectrum to the Ultra-violet.** E. H. KURTH (*Physical Rev.*, 1921, **18**, 461—477).—Certain improvements in technique made it possible to obtain the following values for the convergence wave-lengths in Å.U.: *K* series, carbon 42·6, oxygen 23·8; *L* series: carbon 375, oxygen 248, aluminium 100, silicon 82·5, titanium 24·5, iron 16·3, copper 12·3; *M* series: aluminium 326, titanium 85·3, iron 54·3, copper 41·6; *N* series: iron 247, copper 116. It is suggested that the radiation from solid targets may differ from the radiation from gaseous atoms, especially for the lighter elements. A. A. E.

**The Significance of the Half Terms in Spectral Series Formulæ.** PAUL D. FOOTE and F. H. MOHLER (*J. Opt. Soc. Amer.*, 1922, **6**, [i], 54—56).—The ratio of the constant $a^*$ for the enhanced spectrum of an alkali earth to the constant $a$ for the arc spectrum of the alkali with the next lower atomic number has been computed on the basis of the quantum theory and compared with the observed values. W. E. G.

**The Occurrence of Spark Lines (Enhanced Lines) in the Arc. II. Magnesium, Zinc, and Cadmium.** G. A. HEMSALECH and A. DE GRAMONT (*Phil. Mag.*, 1922, [vi], **43**, 834—871; cf. this vol., ii, 176).—Further experimental observations have been made on the spectra observed in liquid and vacuous film arcs and in arcs surrounded by gaseous media. The results point to the existence of four distinct stages in the spectral development of the arc flash (1) the film stage during which the spark lines are enhanced and symmetrically broadened, (2) a short region marked by the strong emission of spark lines, (3) a stage during which the spark lines are but feebly emitted and at the end of which their emission ceases abruptly, and (4) the last period of the flash during which arc lines are alone emitted. The flashing up of the spark lines and their symmetrical broadening at the instant of striking the arc is shown to be due to the momentary establishment of a powerful electric field between the electrodes. The symmetrical broadening of the lines is believed to be due to the Stark effect.

The disappearance of the magnesium spark line λ 4481 at a definite point during the second phase occurs when the electric field is reduced below 500 volts/cm. The spark lines are brought out prominently in liquid air and disappear when the temperature is raised. It is thus impossible to regard these as high temperature lines. The only types of magnesium lines which are emitted in the absence of electrical or special chemical actions are the flame line λ 4571 and the series triplets. A summary of the relative sensitiveness of the various magnesium lines to electrical and chemical actions is given. W. E. G.

**The Spectrum of Glucinum Fluoride.** SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1921, [*A*], **101**, 187—194).—The previous investigation on the band spectra of the fluorides of magnesium, calcium, strontium, and barium (cf. A., 1921, ii, 529) has been extended to a study of the spectrum of potassium glucinum fluoride. The presence of potassium does not interfere with the band spectrum of glucinum fluoride, neither does glucinum oxide present spectra in the vicinity of the fluoride bands. There are six groups of bands all in the ultra-violet between λ 2800 and λ 3400 and all fading towards the red. The strongest band at 3009 was selected for a detailed investigation, and it was shown to consist of three series of lines which depart from the ordinary formulæ. Each group of glucinum fluoride bands is composed of alternating double and single heads, and this is the only similarity they present to the spectra of the other alkaline-earth fluorides. The formula, given in the previous paper for the $E_1$ group of magnesium fluoride gives satisfactory agreement for the glucinum fluoride bands.
W. E. G.

**Emission Bands of Erbium Oxide.** E. L. NICHOLS and H. L. HOWES (*Science*, 1922, **55**, 53).—A confirmation of the work of Mallory (*Physical Rev.*, 1919, **14**, 54). At temperatures at, or slightly below, 1000°, there are three regions, in which the principal emission bands of the spectrum of erbium oxide are situated, which are brighter than for an ideal black body at the same temperature. A. A. E.

***N*-Series in X-Ray Spectra.** V. DOLEJŠEK (*Nature*, 1922, **109**, 582).—By using Siegbahn's apparatus, lines which most probably must be referred to the *N*-series of uranium and thorium have been detected. Calculations show that for these elements, some of the lines must have wave-lengths of about the measured values (8·6—12·0 Å.U. and 9·4—13·5 Å.U., respectively), whilst for bismuth and the elements in its neighbourhood all the *N*-lines must have a wave-length of more than 13 Å.U. A. A. E.

**Spectrophotometric Study of Solutions of Cupric Chloride.** FREDERICK H. GETMAN (*J. Physical Chem.*, 1922, **26**, 217—246).—The extinction coefficients of a series of solutions of cupric chloride (2·622—0·8443*M*) have been determined at 28·3° for various wave-lengths lying between 460 μμ and 560 μμ. A further series of extinction coefficients of a number of binary mixtures of cupric

chloride with hydrochloric acid, potassium chloride, lithium chloride, calcium chloride, aluminium chloride, and zinc chloride, respectively, have also been determined over the same region of the spectrum; in each case the concentration of the copper salt was kept constant (0·8443*M*), whilst the concentration of the added chloride was progressively increased. It is shown that in solutions of cupric chloride, Beer's law holds only in the region of longer wave-lengths, and that in this region both ions and undissociated molecules may be assumed to possess nearly equal absorbing powers. No apparent relation has been found to exist between absorption and dissociation; in fact, no satisfactory interpretation of the mechanism of the absorption of light by electrolytes seems to be possible, unless the view of Hantzsch be adopted, that absorption is independent of dissociation. The absorption of light by solutions of cupric chloride has been attributed to the presence of complex ions, the composition of which is conditioned, primarily, by the concentration of the solution. In extremely dilute solutions, absorption is assumed to be due to the presence of copper atoms holding in combination as many molecules of solvent as correspond with the co-ordination number of the metal, which, in this case, is four. In extremely concentrated solutions, complex anions containing copper have been shown to be present, and to these the hypothetical formula $CuCl_4''$ has been assigned. Other complex ions, in which one, two, or three of the water molecules of the tetrahydrated copper-ion have been replaced by chlorine atoms, are assumed to be present in solutions of intermediate concentrations. A study of the absorption spectra of the metal ammines has shown that substitution of a chlorine atom for a water molecule in a complex ion causes a displacement of the minimum in the absorption curve toward the red end of the spectrum. Increase in concentration, or the addition of colourless chlorides, is shown to displace the absorption minimum of 0·8443*M* cupric chloride toward the red end of the spectrum. The cause of the observed displacement of the absorption minimum is believed to be the same as in the case of the metal ammines, namely, the successive replacement of water molecules by chlorine atoms in complex ions. J. F. S.

**Absorption of Light by Solutions of Cupric Lithium Chloride.** FREDERICK H. GETMAN (*J. Physical Chem.*, 1922, **26**, 377—383).—The absorption of light by solutions of cupric lithium chloride ($CuCl_2,LiCl,2H_2O$) has been examined spectrophotometrically, and the resulting absorption curves have been compared with corresponding curves for cupric chloride. The minima in the absorption curves were found to lie nearer the red end of the spectrum than the corresponding minima in the curves obtained with solutions of cupric chloride. In dilute solutions, the absorption curves of cupric lithium chloride and cupric chloride were found to be identical. From a comparison of the conductivities of solutions of cupric lithium chloride with the sum of the conductivities of cupric chloride and lithium chloride at the

same dilutions, it is found that the double salt, when dissolved in water, undergoes almost complete dissociation into the two component salts. The possibility suggested by Donnan that the solid salt may undergo dissociation as indicated by the equation $CuCl_2,LiCl,2H_2O \rightleftharpoons (Li2H_2O)^+ + (Cu3Cl)^-$ (A., 1905, ii, 806) is emphasised as offering a satisfactory explanation of the fact that the colour of the compound is widely divergent from that characteristic of copper salts. J. F. S.

**Absorption Spectra of Glasses of Various Composition containing Didymium.** F. WEIDERT (*Z. wiss. Photochem.*, 1922, **21**, 254—264).—A spectrographic comparison of the absorption spectrum of didymium present as a solid solution in various glasses with that of aqueous solutions of the nitrate of didymium and other rare earths, and an investigation of the effect of the composition of the glass on the absorption spectrum. Eight of the glasses investigated contained various amounts of four or five of the oxides of silicon, boron, arsenic, lead, aluminium, calcium, potassium, and sodium, together with a mixture of the oxides of neodymium, praseodymium, samarium, cerium, and lanthanum. The remaining glass contained pure neodymium oxide. The aqueous solutions employed for comparison included, not only a solution of the mixture referred to, but also solutions containing respectively the equivalent of 1·37 gram of neodymium oxide, 0·76 gram of praseodidymium oxide, and 0·42 gram of samarium oxide per litre. The absorption bands characteristic of the glasses were broader and less sharp than the corresponding bands afforded by the aqueous solutions. The presence of boron in the glass increased the want of sharpness of the bands. Lead–potash glasses afforded the sharpest bands. Reproductions of certain of the absorption spectra are given, and the paper discusses the shift of the bands in various cases. J. S. G. T.

**The Absorption of Colouring Matters of the Flavone Group. II. Absorption Spectra of Phenyl Styryl Ketone and its Derivatives.** YÛJI SHIBATA and WILLY NAGAI (*J. Chem. Soc. Japan*, 1922, **43**, 101—122).—To determine the effect of the hydroxyl group on the absorption of light in compounds intimately related to the flavone group, the authors have studied the absorption spectrum of phenyl styryl ketone and its hydroxyl derivatives. Phenyl styryl ketone in $0·0001N$-alcoholic solution shows a large absorption band in the ultra-violet (the centre being $\lambda$ 3·300). The absorption of flavone, therefore, is more hypsochromic than that of phenyl styryl ketone in the same concentration (cf. Shibata and Kimotsuke, *J. Chem. Soc. Tokyo*, 1918, **39**, 771). The effect on the absorption of light of the introduction of the hydroxyl group into phenyl styryl ketone is more complex than in the case of flavone. The effect of the introduction of the hydroxyl group into the phenyl group is very small; whilst in the styryl group it is distinct. In the latter case, it is bathochromic and accompanies the appearance of one or two new absorption bands. By introducing the hydroxyl group into both the phenyl and styryl groups

at the same time, the band is enlarged, and is bathochromic. When two hydroxyl groups are introduced into the group, the effect is additive, except in some cases of ortho-replacement. From the point of view of light absorption, natural naringenin is not shown to be a derivative of phenyl styryl ketone. K. K.

**Spectrographic Detection of Change in Blood Pigment due to certain Organic and Inorganic Poisons, and the Characteristic Spectra of Yolk of Egg and Urobilin.** L. LEWIN and E. STENGER (*Z. wiss. Photochem.*, 1922, **21**, 221—226; cf. A., 1908, ii, 1048).—In continuation of previous work, the authors have investigated photographically the effect of hydrocyanic acid, phenylhydrazine, acetylene, hydrogen phosphide, and sulphurous acid on the absorption bands of blood, both when the poison was added to blood withdrawn from an animal and when the poison was injected into the living animal. Only in the case of addition of phenylhydrazine did any appreciable shift of the absorption bands occur. In the case of blood derived from a rabbit after injection of phenylhydrazine, absorption bands occurred at $\mu\mu$ 629, 609, 581, 557, and 402, compared with absorption bands at $\mu\mu$ 577, 537, and 415 for normal blood. In the case of hydrocyanic acid, whilst no appreciable shift of the bands occurs, the sharpness of the bands diminishes, at first slowly, as the percentage of hydrocyanic acid increases. The absorption spectrum of yolk of egg showed bands at $\mu\mu$ 482, 453, 429, 401, and 380. The absorption spectrum of preparations of urobilin showed a band in the region $\mu\mu$ 494. By addition of an alcoholic solution of zinc chloride and ammonia, the maximum intensity in the band moves to $\mu\mu$ 509 and the solution fluoresces. J. S. G. T.

**Optical Rotatory Dispersion. II. Tartaric Acid and the Tartarates.** THOMAS MARTIN LOWRY and PERCY CORLETT AUSTIN (*Phil. Trans.*, 1922, [*A*], **222**, 249—308).—Bakerian lecture. The rotatory power of tartaric acid for a series of nine wave-lengths has been determined in aqueous solutions of eleven different concentrations ranging from 5 to 55% by weight, and also for twenty-one and twenty-six wave-lengths, respectively, at two other concentrations. The optical rotatory power of tartaric acid, like those of its methyl and ethyl esters, is expressed to a close degree of approximation by the formula $\alpha=k_1/(\lambda^2-\lambda_1^2)-k_2/(\lambda^2-\lambda_1^2)$. The rotatory power of sodium tartrate agrees very closely with Biot's law, $\alpha=k/\lambda^2$, but requires for its exact expression a two-term formula similar to that used for tartaric acid. Potassium and ammonium tartrate and Rochelle salt give similar dispersion curves, but deviate more widely from Biot's law. A number of solutions which give negative rotations have been examined for a range of wave-lengths and the corresponding dispersion curves have been plotted. In the presence of an excess of boric acid, the rotatory dispersion of tartaric acid is no longer complex but simple, and may be expressed over a wide range of wave-lengths by the equation $\alpha=k/\lambda_2^2-\lambda_0^2$. Tartar emetic also gives a simple dispersion curve. When tartar emetic is dissolved in an excess of potassium hydroxide,

r when a corresponding solution is prepared with bismuth in place f antimony, strongly lævorotatory solutions are obtained, but iese again are characterised by a simple rotatory dispersion. ; is suggested that tartaric acid, like nitrocamphor, exists in ›lution in two labile isomeric forms, and that the anomalous spersion of the acid and of many of its derivatives is due to the ·esence of two isomeric compounds of opposite rotatory power id unequal dispersion. Derivatives which give simple rotatory spersion are assumed (like salts of nitrocamphor) to be fixed ı one of these forms. J. F. S.

**The Inversion of the Rotatory Power in Anisotropic Liquids.** . Royer (*Compt. rend.*, 1922, **174**, 1182—1185).—Cholesteryl nnamate shows inversion of its rotatory power. The wave-ngth at which this inversion occurs varies with the temperature, ıe wave-length increasing as the temperature decreases. The ave-length of the reflected light varies with the temperature in ıe same manner, and it would appear that these two wave-lengths ·e identical. W. G.

**Phototropy of Inorganic Salts. Cuprous Chloride and romide.** Gopal Singh (T., 1922, **122**, 782—785).

**Conversion of Energy in Photochemical Processes.** A. yk (*Z. wiss. Photochem.*, 1922, **21**, 197—199).—The contributions Grotthus and of Draper to the theory of photochemical processes ·e briefly reviewed, and attention is directed to outstanding nbiguities in the application of Einstein's quantum photochemical w to such processes. J. S. G. T.

**Velocity of Reaction in the Photochemical Dissociation of ›rric Chloride.** E. Puxeddu and F. L. Vodret (*Gazzetta*, ›22, **52**, i, 229—234; cf. A., 1920, ii, 406).—The velocity of ·composition of ferric chloride in ethereal solution according the equation $FeCl_3 = FeCl_2 + Cl$ has been measured under ırious conditions, both sunlight and electric arc light being ›ed to effect the reaction. The course of the reaction was fol-wed by titrating the ferrous salt with permanganate in presence a few c.c. of Zimmermann's solution. As far as a certain stage the reaction, the latter follows the equation for unimolecular actions. The change proceeds more slowly in arc light than in nlight, and yields a dense, highly transparent precipitate of rrous chloride. T. H. P.

**An Attempt to Detect Induced Radioactivity resulting om α-Ray Bombardment.** A. G. Shenstone (*Phil. Mag.*, ›22, [vi], **43**, 938—943).—It is shown that the violent dismember-ent of a molecule by an α-particle does not give rise to unstable ıclei, capable of emitting mass particles of a range greater than 0 mm. Also no cumulative effect is observable after a heavy ›mbardment by the α-particles. These negative results do not ·eclude the possibility of radioactive disintegrations taking place hich involve the emission of β-particles or γ-radiation. W. E. G.

**The Production of β-Ray Spectra by Radioactive Substances.** LISE MEITNER (*Z. Physik*, 1922, **9**, 131—144).—Experiments on the β-ray spectra of thorium-*B* have shown that it is possible to distinguish between a primary β-ray emitted from the nucleus and a secondary β-spectrum from the *K* and *L* rings of electrons. The primary β-rays are supposed to be converted into γ-rays in the nucleus and these set free electrons from the envelope of the atom. The source of the secondary β-rays was ascertained by allowing the γ-rays from thorium-*B* to set free electrons from an isotopic element, namely, lead, and comparing the velocities of these electrons with those emitted from the radioactive element. Two groups of β-rays were emitted identical with those from thorium-*B*. The energy of the γ-rays calculated from the energy of the secondary electrons, and the work required to separate these electrons from the nucleus, were found to agree with a wave-length $\lambda_\gamma=5{\cdot}2\times10^{-10}$ cm. and with a velocity for the primary β-ray of 73·9%. This β-ray was found to be present in the spectra emitted from thorium-*B*. The intensity was, however very small, so that the primary β-ray emission is almost entirely converted into γ-rays. Evidence of the presence of electrons from the *K*, $L_1$, and $L_2$ rings was found. Similar conclusions are drawn for other elements, but the β-spectra of radium and radiothorium are entirely secondary in origin. The velocity of the primary β-ray, the atomic weight, and the life period of the isotopes of lead, radium-*B*, thorium-*B*, and radium-*D* are shown to be intimately related. W. E. G.

**The Relationship between β- and γ-Rays.** LISE MEITNER (*Z. Physik*, 1922, **9**, 145—152; see preceding abstract).—Arguments are adduced for the conclusion that γ-rays from radioactive substances have their origin in the nucleus. From the behaviour of uranium-*X* and radium-*C*, it is concluded that the primary β-ray is intense only when the γ-ray emission is small. The results of Ellis (A., 1921, ii, 422) on radium-*B* preparations are explained on the assumption that there are three γ-ray frequencies emitted from the nucleus, two of which correspond with two different primary β-rays. The middle γ-ray could be accounted for if the most rapid β-ray under certain conditions gave up part of its energy and left the nucleus with the remainder. W. E. G.

**Reflection of *X*-Rays from Imperfect Crystals.** C. G. DARWIN (*Phil. Mag.*, 1922, [vi], **43**, 800—829).—In the recent work of Bragg, James, and Bosanquet (A., 1921, ii, 477) on the reflection of *X*-rays from crystals, use was made of the theoretical formulæ of the author. The position of the electrons in a crystal can be inferred from a study of the intensity with which the various faces of a crystal reflect a given wave-length. The problem falls into two stages, the first from crystal to molecule and the second from molecule to electron. The formulæ are, however, falsified by the phenomenon of extinction. Extinction is shown to lead to two types, primary and secondary. The primary diminishes the reflection from a perfect crystal below the amount given by the

simpler theory. This is, however, negligible for crystals invisible under a high-power microscope. The reflection from a small, perfect crystal, a conglomerate composed of a large number of small crystals oriented in nearly the same direction, and crystal powders is examined, and formulæ are worked out for $Q$, a quantity which is, approximately, the amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. W. E. G.

**Positive Ray Analysis of Lithium and Magnesium.** A. J. DEMPSTER (*Physical Rev.*, 1921, **18**, 415—422; cf. *ibid.*, 1918, **11**, 316; *Science*, 1920, **52**, 559).—Lithium has two isotopes with atomic weights 6 and 7, respectively, the relative proportions of which vary with the conditions. A suggested possible explanation is that the rates of evaporation of the two isotopes vary with the surface conditions of the metal. Magnesium has three isotopes with atomic weights 24, 25, and 26, the relative proportions being 7 : 1 : 1. These ratios give a mean atomic weight of 24·336. A. A. E.

**The Disappearance of Gas in the Electric Discharge. IV.** THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LONDON (*Phil. Mag.*, 1922, [vi], **43**, 914—937; cf. A., 1920, ii, 730; 1921, ii, 369, 533).—A further account of experiments on the disappearance of gas in the presence of phosphorus vapour. The decrease in pressure was measured by use of a lamp filament as the hot wire of a Pirani gauge and by determining whether the pressure is above or below the value at which the glow potential is equal to the applied potential. The amounts of hydrogen adsorbed increase with increase in the phosphorus introduced. A marked step in the adsorption, however, occurs for 0·09 to 0·27 mg. of phosphorus. Sodium fluoride and phosphorus together exert a greater effect than either substance singly; spluttered tungsten is also effective. The adsorption of gases takes place in two stages; the first is practically instantaneous and is impossible to control.

The solid films on the walls are possibly in an electrically polar condition, and it is suggested that gaseous ions enter into combination with the surface by virtue of their charges. The very small adsorption of inactive gases, which do not form negative ions, suggests that it is the negative ions which are adsorbed by this layer. W. E. G.

**The Potential of the Iodine Electrode and the Activity of the Iodide Ion at 25°.** A. MCKEOWN (*Trans. Faraday Soc.*, 1922, **17**, 517—521).—*E.M.F.* measurements have been made for cells of the type $Pt+I_2|KI$ solution sat. with $I_2|$sat. $KCl|N$ calomel electrode, the concentration of potassium iodide being varied between wide limits. From the results, the activities of the iodide-ion and the tri-iodide-ion in the various solutions have been calculated. It was found that the activities of both ions increased much less rapidly than their concentrations. The potential of the normal

(saturated) iodine electrode has been deduced in terms of the activity of the iodide-ion. The value found is +0·2454 volt, the normal calomel electrode being taken as zero. W. T.

**The Effect of Telluric Acid on the Potential of a Silver Anode.** FRANZ JIRSA (*Z. Elektrochem.*, 1922, **28**, 186—191).—The author has determined the effect of halogen ions on the potential of a silver anode, and has investigated the nature of the depolarisation effected by telluric acid. In general, the halogens depolarise a silver anode in an alkaline electrolyte and reduce the value of the decomposition voltage. Apart from the fluorine-ion, which exerts no depolarising effect in an alkaline electrolyte, the maximum depolarisation is effected by the iodine-ion, the minimum by the chlorine-ion. Fluorine-ions accelerate the appearance and evolution of oxygen at the anode. When the polarisation of a silver anode in an alkaline electrolyte containing halogen ions is a maximum, the dioxide, $Ag_2O_2$, alone is formed. The monoxide, $Ag_2O$, is produced when a silver anode is polarised to +1·40 volts in an alkaline electrolyte containing telluric acid. The following reactions occur: $Ag_2O+K_2TeO_4+H_2O \rightleftharpoons Ag_2TeO_4+2KOH$; $2Ag_2O_2+2K_2TeO_4+2H_2O \rightleftharpoons 2Ag_2TeO_4+4KOH+O_2$. The potential of the electrode $Pt/Ag_2O_3$ in an alkaline electrolyte containing telluric acid is constant and equal to 1·57 volts. J. S. G. T.

**Effect of Changing the Hydrogen-ion Concentration on the Potential of the Zinc Electrode.** THEODORE W. RICHARDS and THEODORE DUNHAM, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 678—683).—Measurements of the potential of zinc in acid solutions of zinc sulphate, of various concentrations, measured at 18° against the calomel electrode, through a sodium sulphate bridge, and also directly against a zinc electrode containing pure *N*-zinc sulphate solution, showed marked rise in potential as the acid concentration was increased. The magnitude of this rise in potential indicated that it must be due partly to the liquid junction potential, owing to the presence of the hydrogen-ion. Equal concentrations of the sulphate-ion in the form of alkali sulphates added to the zinc sulphate solution gave smaller elevations in the potential, which elevations were in the order of the transport numbers of the kations concerned. It is assumed that the change in liquid junction potential produced by sodium sulphate is small and therefore it may be inferred that about two-thirds of the change produced by sulphuric acid is due to solution junction potential and the remaining third to a real increase in the single electrode potential of zinc, due, presumably, to the depression of the electrolytic dissociation of zinc sulphate. J. F. S.

**Variations in the Conductivity of Solid Electrolytes.** P. VAILLANT (*J. Phys. Radium*, 1922, **3**, 87—100; cf. A., 1912, ii, 419; 1920, ii, 722).—The changes in conductivity of solid electrolytes with temperature are due to two independently varying phenomena; the first of these occurs instantaneously, whilst the second is a slow change, frequently in an opposite direction to the first. These

rogressive changes in the conductivity at constant temperature re not related to phosphorescence, being shown by many types of ılts. The polarisation which occurs on passing the current is aintained indefinitely unless the crystals are short-circuited. he conductivity during the initial period is given by the relation : g $C_T=a+bT$ or $\log C_T=\alpha-\beta/T$. In the second phase, the ıanges in conductivity follow different laws, being manifested by series of oscillations of decreasing amplitude. W. E. G.

**Abnormality of Strong Electrolytes and the Ionisation 'heory of Ghosh.** JAMES KENDALL (*J. Amer. Chem. Soc.*, )22, **44**, 717—738).—The ionisation hypothesis put forward by hosh to explain the abnormality of strong electrolytes (T., 1918, **13**, 449, 627, 707, 790; 1920, **117**, 823, 1390) has been critically ıalysed and the following conclusions have been drawn. The cond and third postulates are absolutely incompatible, for if the articles of a salt in solution possess a definite space-lattice arrange-ıent, as in the crystalline state, then the combination of two ppositely charged particles to form a salt molecule or a completely turated electrical doublet is impossible. Ghosh's calculation of ıe electrical work required to separate the component radicles of gram-molecule of a dissolved salt is erroneous. The value actually ərived, assuming a cubic space lattice arrangement, exceeds that ɔtained by Ghosh by 75%. The experimental conductivity data r potassium chloride solutions are not in agreement with the uation which Ghosh obtains from his postulates, or with various ırrected forms of this equation. The agreement claimed by hosh to exist between his equations and the experimental results previous investigators is largely fictitious. The remarkable incidence of calculated and observed values in many tables is ıe to far too frequent errors of calculation and transcription. In her cases, the only legitimate deduction is that the equations sted serve very well as interpolation equations over a restricted nge. No confirmation of the theory of Ghosh is afforded by the perimental data for (*a*) the variation of equivalent conductivity ith dilution for salts in aqueous solution, (*b*) the temperature efficient of the ratio $\mu_v/\mu_\infty$, (*c*) the electrical conductivity of ɔn-aqueous solutions, (*d*) the molecular number *i* and the Clausius eorem, (*e*) the ionisation of strong acids, (*f*) the ionisation of əak acids, (*g*) the ionisation of transition acids, (*h*) the electrical nductivity of pure salts in the solid and fused states, (*i*) the nductivity of salts in mixtures of pyridine and water, (*j*) the nisation of salts in solvents of low dielectric constant, (*k*) the ırtition of a salt between an ionising and a non-ionising solvent, ıd (*l*) the vapour pressure of the hydrogen haloids in aqueous lution. The rôle of the solvent in ionisation, which is ignored together by Ghosh, must be taken into account in any complete pothesis of conducting solutions. In its present form, the nisation hypothesis of Ghosh is unacceptable, and certain of the əstulates on which it is based must be either modified or rejected. J. F. S.

**Ionic Equilibria of Strong Electrolytes.** ALLEN E. STE. (*J. Amer. Chem. Soc.*, 1922, **44**, 670—678).—The equivalent c ductivities of the haloids of sodium and potassium of vary weight normal concentrations (0·1—4·0*N*) have been determi at 25°. A series of similar determinations has also been m for mixtures of a sodium and a potassium haloid. The obser values for the mixed salt solutions have been compared with th calculated from the values for the pure salt solutions at equiva total concentrations on the basis of the isohydric principle. ' differences between the calculated and observed values were fo to be positive and to increase with the total salt concentration with the numerical value of the ratio of sodium to potassium in the mixture, but to decrease generally from chloride to iod In general, the results are to be explained on the basis of comp formation, although at present no explanation is offered for seeming decrease in complex formation on proceeding from chlor to iodides. Tables of the specific gravities and the relative cosities of all solutions measured are given in the paper. J. F. S

**Influence of the Solvent on Ionisation and the Accompa ing Heat Effect.** SIDNEY MAURICE NEALE (*Trans. Fara Soc.*, 1922, **17**, 505—516).—In passing from pure water as solv to 93·8% acetone, the ionisation constant of picric acid falls fr about 0·2 to 0·002, but even in the latter case the deviation fr Ostwald's dilution law still manifests itself, and, to a sim extent, the value of *k* decreasing by about 50% on increasing dilution from 32 to 1024 litres. In anhydrous acetone, the ioi ation constant for picric acid has fallen to the order of 1 and Ostwald's dilution law is obeyed. This indicates that anomaly of strong electrolytes is to be referred to some prope of the system solute plus solvent, rather than to high degree dissociation. The heat of ionisation of picric acid varies larg with the nature of the solvent, passing through a minimum about 70% acetone. In the case of *p*-nitrobenzoic acid, the h of ionisation is practically zero. In 44·35% acetone, the ionisat constant has fallen one-twentieth of its valne in pure water, l the heat of ionisation is still zero. W. T

**The Hydrolysis of a Salt formed from a Weak Acid a a Weak Base.** R. O. GRIFFITH (*Trans. Faraday Soc.*, 1922, 525—527).—A theoretical paper. The author points out that is necessary to state more exactly what is meant by the "deg of hydrolysis" in the case of a salt of a weak acid and a we base at great dilution. He shows in the case of aniline acetate t at a dilution of 5000 litres the concentration of undissociated a is not equal to the concentration of undissociated base, that the degree of hydrolysis differs for each ion. The calculation a shows that the hydrogen-ion concentration, whilst practica constant down to $v=500$ (the limit of Tizard's measurements ( 1910, **97**, 2494), should not be independent of the concentrati between $v=500$ and $v=5000$, but should fall with increas dilution. W. T

**[Biochemical and Electrochemical Oxidation of Organic Compounds.]** A. NATHANSOHN (*Z. Elektrochem.*, 1922, **28**, 129—130).—A criticism of the views put forward and the interpretation of the author's work (*Koll. Chem. Beihefte*, 1919, **11**, 261) by Fichter in a paper under the same title (this vol., ii, 23).

J. F. S.

**Simple Formula for the Calculation of the Specific Heats of Solids.** H. J. KRASE (*J. Amer. Chem. Soc.*, 1922, **44**, 784—786).—A simple form of the specific heat equation of Lewis and Gibson (A., 1918, ii, 29), $C_v = f(T/\theta)$ has been obtained which fits the experimental facts. This equation has the form $C_v = 2{\cdot}91 + 2{\cdot}89$ tan h $2{\cdot}95 \log T/\theta$. Since the entropy equation is obtained by integration of the specific heat equation $S_v = \int(2{\cdot}91 + 2{\cdot}89 \tanh 2{\cdot}95 \log T/\theta) d \log_e T/\theta$, and on evaluating the integration constant by putting the entropy equal to the Lewis-Gibson value 1·62 when $\log T/\theta = 0$, $S_v = 6{\cdot}70 \log T/\theta + 5{\cdot}18 \log \cosh 2{\cdot}95 \log T/\theta + 1{\cdot}62$.

J. F. S.

**Polymerisation at the Critical Temperature.** WILLIAM R. FIELDING (*Chem. News*, 1922, **124**, 182—184, 198—199, 215—217; cf. A., 1920, ii, 732; A., 1921, ii, 487).—Calculations are made of the polymerisation factor at the critical temperature for a large number of volatile organic and inorganic compounds.

W. E. G.

**Cinnamic Acid in Cryoscopy.** P. FALCIOLA (*Gazzetta*, 1922, **52**, i, 175—179).—The results furnished by anthracene, naphthalene, *o*-, *m*-, and *p*-nitrobenzaldehydes, and phenylpropionic and phenylpropiolic acids differ somewhat from those obtained by Mathews (A., 1917, ii, 356) and show that the value of the cryoscopic constant for cinnamic acid is about 100. The fact that phenylpropionic acid, when dissolved in cinnamic acid, produces almost normal depressions of the freezing point confirms Bruni's conclusion (A., 1899, ii, 731; 1900, ii, 714) that there is no tendency to the formation of solid solutions when saturated compounds are dissolved in unsaturated ones, although such tendency is exhibited in the inverse case (cf. also Mascarelli and Pestalozza, A., 1907, ii, 936; 1908, i, 527). T. H. P.

**A Micro-method for the Determination of Molecular Weight in a Melting-point Apparatus.** KARL RAST (*Ber.*, 1922, **55**, [*B*], 1051—1054).—The freezing point of camphor is depressed to such an unusual extent by the presence of dissolved substances that the effects can be measured with sufficient accuracy for the determination of molecular weight by means of an ordinary thermometer and with minute amounts of material.

The substance under investigation and the camphor are weighed into a small tube which is subsequently closed with a cork carrying a pointed needle. The substances are melted together, well mixed, allowed to solidify, and withdrawn by means of the needle. A portion of the mixture is transferred to a melting-point tube the

bottom of which must be semi-spherical; it is pressed firn together, giving a compact column not exceeding 1 mm. in heig The tube is heated in the usual melting-point apparatus. T mixture rapidly assumes the appearance of melting ice and later converted into a cloudy liquid in which the presence of delicate crystalline skeleton can be sharply detected by means a lens. As the temperature rises, the latter disappears from abo downwards, and the point at which the last trace vanishes recorded as the melting point. Since the readings required ε differential, the use of normal thermometers and the correction i the exposed part of the thread are unnecessary. H. W.

**Orientation of Molecules in Surfaces. VII. Vaporisati in Steps as Related to Surface Formation.** WILLIAM HARKINS and LATHROP E. ROBERTS (*J. Amer. Chem. Soc.*, 192 **44**, 653—670; cf. A., 1921, ii, 242).—An account is given of t amount of energy involved in the various steps in the process vaporisation, based on the assumption that the surface throu which the vaporisation occurs is not highly curved. The resul are expressed in *micri-ergs* as unit which is defined as $10^{-14}$ erg The relationships found at a corresponding temperature of 0· are tabulated for oxygen, nitrogen, ethyl ether, ethyl acetat carbon tetrachloride, benzene, chlorobenzene, methyl alcohol, ar ethyl alcohol, and the data indicate that, at a definite correspondi temperature, in the case of non-associated liquids the molecul of which are symmetrical, the molecular values for the late heat of surface formation, *l*, the total surface energy, *e*, the energ of thermal emission, *j*, and the internal heat of vaporisation, λ are nearly proportional to the critical temperatures of the liquid The same relation seems to hold for the free surface energy, provided that the temperature range is not too great. Thus th free surface energy of ethyl ether at a corresponding temperatu of 0·7 is 4·0 as calculated from the value for carbon tetrachlorid and 3·9 as calculated from the value for chlorobenzene, whilst th experimental value is 4·0. This statement, as applied to the later heat of vaporisation alone, is somewhat similar to Trouton's law which is known to be not entirely exact. Since the principl expressed above is much more general in its application, it is t be expected that it will prove to be somewhat less exact. Th energy values for ethyl ether are lower than those for carbon tetra chloride, and this is a consequence of the lower critical temperatu of the ether. The effect of a lack of symmetry in the molecul especially when marked, is to lower the molecular free surfac energy, latent heat of surface formation, and total surface energ and to increase the energy of thermal emission. Values are calcul ated for ethyl alcohol from the critical temperature on the assump tion of a symmetrical molecule, using the values of carbon tetra chloride as a basis, and from the actual results it is evident tha the molecular free surface energy, the total surface energy, an more markedly the latent heat of surface formation are considerabl lowered by the dissymmetry of the molecule. The most strikin

effect is, however, the very great increase in the energy of thermal emission. The symmetry considered is that of the electro-magnetic forces round the molecule rather than a symmetry with respect to mass. The substitution of the slightly polar chlorine atom for hydrogen in benzene gives almost exactly the calculated value for a symmetrical molecule except in the case of the thermal emission, which is considerably increased, since it is the most sensitive of all the quantities to changes of molecular symmetry. Since $e$ is decreased and $j$ increased by increasing dissymmetry of the molecule, the ratio $e/j$ serves as a remarkably sensitive index of molecular symmetry. The ratio $e/\lambda$, which is equal to $e/(e+j)$, varies in the same way, but not to so large an extent. According to Stefan's law, the ratio of the total energy necessary to carry a molecule from the interior of a liquid into the surface to its total heat or energy of vaporisation, $e/\lambda$, is equal to 1/2. This is shown not to be the case. Not only is this an increasing function with increasing symmetry of the molecule, but also with increasing corresponding temperature. Its value appears to approach unity as the corresponding temperature approaches unity. Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapour phase than when the corresponding temperature is low. The *relationships noted above are just those indicated by the hypothesis* that molecules in the surface are oriented, the orientation increasing *with increasing dissymmetry, and decreasing with increasing* thermal agitation. The effect of thermal agitation is illustrated *in the case of the alcohols; compounds of the polar–non-polar type.* It is shown for these compounds that the molecular surface energy *increases with the temperature. The effect of increased agitation* is to overcome the orientation partly, and to throw the more polar *groups into the outer surface, thus increasing the surface energy.*

J. F. S.

**Vapour Pressure of Sulphur Dioxide and Ammonia.** F. W. Bergstrom (*J. Physical Chem.*, 1922, **26**, 358—376).—The vapour pressure of ammonia and sulphur dioxide has been determined at temperatures from slightly above the normal boiling point to the freezing point. An improved form of apparatus is described which is capable of giving vapour pressure measurements below 900 mm. at low temperatures. The measurements are compared with those of Burrell and Robertson (A., 1916, i, 6; ii, 81) and of Brill (A., 1906, 847), and it is found that the author's results are in keeping with the Ramsay-Young relationship, whilst those of Brill and of Burrell are not. It has been shown experimentally that Burrell's vapour pressure measurements for ammonia are erroneous. The triple point of ammonia has been found to lie at −77·9° at a pressure of 45·5 mm. The value found by Cragoe, Meyers, and Taylor (A., 1920, ii, 370) is −77·70 at 44·9 mm.

J. F. S.

**Binary Liquid Mixtures.** O. Faust (*Z. physikal. Chem.*, 1922, **101**, 94—103).—A theoretical paper in which, for the purpose

of comparing the relative efficiency and accuracy of the static and dynamic methods of determining the vapour pressure of liquid mixtures, the author has recalculated the results obtained by Schmidt (this vol., ii, 119), Beckmann and Faust (A., 1915, ii, 143), and von Zawidzki (A., 1901, ii, 6) for the vapour pressure of mixtures of acetone and chloroform. Curves are constructed and the shape of the curves discussed in connexion with Dolezalek's theory of liquid mixtures. J. F. S.

**Vapour Pressures of Binary Mixtures.** H. CASSEL (*Z. physikal. Chem.*, 1922, **101**, 104—108).—A theoretical paper in which the author criticises mathematically the assertion of Schmidt (this vol., ii, 119) that Dolezalek's theory of liquid mixtures cannot be maintained. The author shows that the measurements of Schmidt for mixtures of benzene and toluene show divergences from a straight line curve which vary between 1·0 and 2·4%. It is shown that the simplicity of Dolezalek's theory in comparison with the complicated expressions of van der Waals and Jahn has justified itself in numerous cases, so that its heuristic significance as a usable working hypothesis cannot be denied (cf. preceding abstract). J. F. S.

**Binary Liquid Mixtures.** ALFRED SCHULZE (*Z. physikal. Chem.*, 1922, **101**, 109—116).—A theoretical paper in which the author criticises the assertions of Schmidt (this vol., ii, 119) and shows that his statements in connexion with Dolezalek's theory of liquid mixtures cannot be maintained. Further, the results on which Schmidt bases his assertions are a confirmation of the theory (cf. preceding abstracts). J. F. S.

**A Continuous Flow Calorimeter, and the Determination of the Heat of Neutralisation of a Solution of Hydrochloric Acid by One of Sodium Hydroxide.** FREDERICK G. KEYES, LOUIS J. GILLESPIE, and SHINROKU MITSUKURI (*J. Amer. Chem. Soc.*, 1922, **44**, 707—717).—A continuous flow calorimeter has been so developed that measurement of the rise of temperature for ten different rates of flow leads to a value of the heat of neutralisation, which is associated with an error, as calculated by the method of least squares, which is less than 0·1% of the heat change itself. It is shown that a few slight modifications in the calorimeter will probably increase the precision. For the heat of neutralisation resulting in the formation of $NaCl,521H_2O$ (about 0·107*N*-sodium chloride) at 32·3°, the value 13280 cal./mol. is found. In the calculation, the specific heat data of Richards and Rowe were used, so that the unit is the 18° calorie (equivalent to 4·18 joules). It is held that this value is accurate within about 0·3%, although it is 2·6% higher than the corresponding point on Wörmann's curve for the same neutralisation (*Ann. Physik*, 1905, [iv], **18**, 775). The present value leads to a value for the heat of ionisation which is chout 0·5% lower than the corresponding point on Noyes, Kato, the Sosman's curve (A., 1910, ii, 257). In the opinion of the more rs, the 1% difference in the heat change when potassium lowere

ydroxide is substituted for sodium hydroxide in the neutralisation ı questionable, because no correction was applied for the carbonate resent. J. F. S.

**Heats of Neutralisation of Potassium, Sodium, and Lithium [ydroxides with Hydrochloric, Hydrobromic, Hydriodic, nd Nitric Acids at various Dilutions.** THEODORE W. RICHARDS nd ALLAN W. ROWE (*J. Amer. Chem. Soc.*, 1922, **44**, 684—707).—'he heat of neutralisation of the four acids by the three bases ıentioned in the title have been determined at a series of dilutions. t is shown that the most serious errors in work of this kind are due ɔ irregularity of mixing, presence of carbonates in the hydroxides, nd inadequate avoidance of loss of heat by cooling. The solutions eutralised were molecular quantities in 100 gram-molecules of water, nd they were combined in all possible pairs over two ranges of emperature not far apart, and the results were interpolated to xactly 20°. The values of the heat of neutralisation obtained anged from 137500 to 14085, sodium hydroxide giving the lowest alues among the bases and hydriodic acid among the acids. With he help of the heats of dilution, of factors and products, previously etermined, the heats of neutralisation at other concentrations have ·een determined, and these have been extrapolated in two ways hrongh a short range to infinite dilution. The heat of formation ·f water from its ions at 20° is found by this short extrapolation to ·e probably not greater than 13·69 $Cal._{20^\circ}$ or 57·22 kilojoules and ·ossibly not smaller than 13·62 $Cal._{20^\circ}$ or 56·93 kilojoules.

J. F. S.

**Pressure Volume Relation of Superheated Liquids.** K. L. VISMER (*J. Physical Chem.*, 1922, **26**, 301—315).—A number of xperiments are described, designed to obtain actual *PV* curves at ıigh temperatures to see whether the curve shows any tendency o bend more sharply as the limit of superheating is approached, and o find what degree of superheating may be attained. Experiments vere made with ethyl ether, ethyl chloride, and *iso*pentane, which vere subjected to a pressure of 20 atmospheres, heated to various emperatures, and the pressure then reduced to 1 atmosphere. The ime before explosion occurred was then noted. In this way, the ıighest temperature to which the liquids may be superheated at ·rdinary pressures was obtained. The values found are ethyl ether 43°, *iso*pentane 136°, and ethyl chloride 126°. The minimum ·ressures which can be reached with liquid ether at temperatures .bove 143° increase with the temperature, the points lying approximately on a straight line joining the critical point with the −72 .tmospheres' point of J. Meyer ("Kenntnis des negativen Druckes in Flussigkeiten," 1911). The pressure–volume relations have been letermined experimentally for liquid ethyl ether at 121·5°, 127·9°, ·nd 133·8°, and for liquid ethyl chloride at 99·6°, 109·7°, and 117·4°, .t pressures down to 1 atmosphere. The pressure–volume relation ınder these conditions is almost linear. There is no tendency ·hown by the *PV* curves to bend more sharply at low pressures as

the limit of superheating is reached. The actual experiments showed a marked departure from van der Waals's curve.

J. F. S.

**The Corresponding States: The Halogenated Derivatives of Benzene.** MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1922, [iv], **31**, 295—299).—In the system of measurements of relativity constituted by the reduced values of the temperature, pressure, and density, the values obtained for the four monohalogenated derivatives of benzene are identical. The properties of the halogens are thus completely masked in such compounds.

For this series of compounds, the relation $M = AD_cT_c/P_c$ holds good independently of the halogen present. $M$ is the molecular weight and $A$ is a constant of value 21·65 for this series. W. G.

**The Determination of Surface Tension from the Maximum Pressure in Bubbles.** SAMUEL SUGDEN (T., 1922, **121**, 858—866).

**Method of Calculating Fluidity, Surface Tension, and Reaction (Equilibrium) Pressure.** HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1922, **193**, 647—655).—A theoretical paper in which it is shown that by means of a formula similar to the Ramsay and Young vapour-pressure equation, it is possible to calculate the fluidity (viscosity) of liquids, the equilibrium pressure of chemical reactions, and the surface tension of liquids. The expression has the form $R'=R+c(T_{B'}-T_B)$, where $R$ and $R'$ are the ratios of the absolute temperatures at which two substances have the same value for any of the properties mentioned, $T_{B'}$ and $T_B$ the temperatures of one of the substances corresponding with the two values of the property chosen, and $c$ is a small constant. The equations have been tested and shown to be in very good agreement with facts. J. F. S.

**The Calculation of Adsorption of Vapours at Different Temperatures.** L. BERÉNYI (*Z. angew. Chem.*, 1922, **35**, 237—238).—On the basis of Polányi's theory of adsorption, a formula has been evolved, by which the equation of state of the adsorbed substance within certain limits of pressure may be approximately calculated. The results for a range of temperatures which extends, for substances boiling between 170° abs. and 400° abs., from 0·06 to 1·4 times the boiling point in degrees abs. show no greater error than that of experimental determination. The formula applies to the reversible and physical adsorption of chemically homogeneous vapours, alone, or from a mixture of comparatively inert gases. From the observed data, $p_1$, or the pressure of the gas, and $x_1$, the quantity adsorbed at a temperature $T_1$, the amount of gas adsorbed at the temperature $T_2$, or $x_2$, may be calculated by the formula: $x_2 = x_1 \times (1 + F_2 - F_1/100)$. $F_2 - F_1 = F$ is a correction factor which takes into account the thermal expansion and the compression of the adsorbed layer. The means by which the value $F$ is determined, with relation to absolute temperature and the variation of the vapour from the law of gases, is given. H. M.

**Electro-adsorption as a Purely Chemical Process.** WOLFGANG OSTWALD (*Kolloid Z.*, 1922, **30**, 254—260).—A theoretical paper in which the author discusses and criticises a paper under the same title by Kolthoff (this vol., ii, 197). It is shown that chemical adsorption, that is, the concentration of a dissolved substance on the surface in consequence of the chemical energy potential existing there, is quite possible. Therefore the hypothesis put forward by Kolthoff (*loc. cit.*) is not a purely chemical hypothesis, but a combination of chemical and electrical hypotheses. The deduction of the well-known adsorption formula by means of the law of mass action leads to concrete practically applicable formulæ only when instead of the stoicheiometric weight concentration of the adsorbing substance the actual reacting mass of this substance is employed. The active quantity corresponds with the sum of the chemically reacting surface layers of the adsorbing substance. The stoicheiometric weight concentration must therefore be multiplied by a factor which connects the actual reacting mass with the total mass. The demand of Kolthoff's hypothesis, that the value of the index must be the same for equivalent adsorbents whilst for electrolytes of different valencies the values stand in a simple relationship to one another, is not in keeping with experimental results. The cases quoted by Kolthoff are accidental or exceptions. In other cases, the hypothesis is in no way confirmed.

J. F. S.

**Diffusion in Porous Vessels.** A. L. HERRERA (*Mem. rev. soc. cient. "Antonio Alzate,"* 1921, **39**, 343—347).—When solutions of reactive salts are allowed to diffuse very slowly together, the precipitates or crystals formed show analogies to natural cells. A solution of potassium silicate, *d* 1·5 or more, containing potassium carbonate not in excess of normality, is placed inside an unglazed porcelain cup, and the latter placed in calcium chloride of *d* 1·0068. After twenty-four hours, numerous very fine tubes of calcium silicate are formed on the outside of the porous cup, bearing on their surface microscopic cells, and in some cases are formed entirely of the latter. CHEMICAL ABSTRACTS.

**An Application of the Optical Method of Determining the Solubility of One Liquid in Another.** C. CHÉNEVEAU (*Compt. rend.*, 1922, **174**, 1019—1021; cf. this vol., ii, 355).—In the case of inorganic or organic salts which are without action on and insoluble in aniline, when their aqueous solutions are in contact with aniline the ratio of the lowering of the refractive index of the aniline to the quantity of water dissolved is constant and the same for equimolecular solutions. The lowering of the refractive index by unit mass is the same for all salts which fulfil the above conditions. W. G.

**Le Chatelier's "New" Geometrical Representation.** ERNST JÄNECKE (*Chem. Ztg.*, 1922, **46**, 361).—A claim for priority against Le Chatelier with regard to the method of geometrical representation of solutions of reciprocal pairs of salts (cf. Jänecke, A., 1906, ii, 833; Le Chatelier, A., 1921, ii, 248). H. W.

**The Partial Miscibility of Liquid Couples. Applicati to Reactions between Dissolved Substances.** RENÉ DUBRI (*Ann. Chim.*, 1922, [ix], **17**, 222—256).—A more detailed acco of work already published (A., 1919, i, 73; ii, 78; 1920, ii, ; 756; 1921, i, 535; ii, 282, 344). W. C

**Sizes of Atoms in Crystals.** ROBERT N. PEASE (*J. A Chem. Soc.*, 1922, **44**, 769—774).—A theoretical paper in wh as an alternative to Bragg's view that the distances between at in crystals can be expressed in terms of atomic radii characteri only of the element concerned, it is suggested that the partic element is of secondary importance for elements the atoms which are of the same rare-gas type, and that the contributior an atom to the distance between it and another atom in a cry depends on the number and arrangement of electrons about positive nucleus, on the type of lattice at least as far as this affe the latter, and, ordinarily, on the magnitude of the charge carr by the atom. The interatomic distances in substances crystallis in the diamond type of lattice have been analysed from this po of view. The following values are recorded: diamond 1·54 (1·5 silicon 2·30 (2·35), grey tin 2·80 (2·80), silicon carbide 1·92 (1·9 zinc sulphide 2·41 (2·35), cuprous chloride 2·41 (2·43), cupr bromide 2·52 (2·57), cuprous iodide 2·66 (2·78), and silver iod 2·80 (3·18). The values in brackets are due to Bragg, and present values generally agree better with the observed val than do those of Bragg. J. F. S.

**Transition from Crystalloid to Colloid Properties with Homologous Series.** EDGAR J. WITZEMANN (*J. Physical Che* 1922, **26**, 201—216).—A theoretical paper in which an attempt made to answer the question "How do such systems as constitu living organisms come into existence?" It is shown that t emulsoid structure of biocolloids (lipoids, carbohydrates, and p teins) constitutes a gross heterogeneity which is also present in much less conspicuous form in the lower crystalloid members the same homologous series. In this way, it follows that t particular properties of biocolloids arise from the cumulative effe of certain groups in the molecule. This effect of chemical co stitution may be easily traced with soaps, but less easily with t carbohydrates and proteins. Associated with the material heter geneity there is a well-known heterogeneity of energy. It is show that such heterogeneities may arise spontaneously on releasir one system into another. The best known energy differentiatio under these conditions is the surface energy. It appears that th surface energy phenomena in solutions are energy differentiatior definitely associated with material differentiations and these i turn are due to chemical constitution, and that changes in th latter necessarily involve the whole series of effects. In connexio with biological phenomena, these two heterogeneities have bee regarded as associated with a vital force, and even now they ar frequently thought to be maintained in organisms by a constan expenditure of energy obtained from chemical reactions in th

organism. It is now shown that certainly part of the heterogeneity occurring in the structure of organisms arises from a predisposition on the part of the component substances themselves to give rise to these effects. Such colloidal systems as those prepared from simple biocolloids are self-reproducing from the components; they arise spontaneously and require no unusual outlay of energy for their construction and maintenance. It is shown that the quantitative statement of Le Chatelier's principle may be easily discovered in the phenomena of true and colloidal solutions so fundamentally involved in biological phenomena. J. F. S.

**Cataphoresis of Colloidal Carbon.** STEPHANIE GOLDBERG (*Kolloid Z.*, 1922, **30**, 230—234).—Colloidal carbon prepared by Sabbatani's method (A., 1914, i, 357; ii, 198) has been thoroughly dialysed to remove sulphuric acid and the influence of various factors on the rate of cataphoresis examined. The sols examined had a specific conductivity at 18° of $22 \cdot 5 \times 10^{-6}$ reciprocal ohms, and had various migration velocities toward the anode from $18 \cdot 3 \times 10^{-5}$ to $13 \cdot 5 \times 10^{-5}$ cm./volt sec. Dilution of the solution increases the velocity slightly to a maximum value, whilst filtration also causes an increase from $18 \cdot 8 \times 10^{-5}$ to $22 \cdot 2 \times 10^{-5}$ cm./volt sec. The addition of acids, irrespective of their nature, causes a decrease in the velocity; thus $0 \cdot 001M$-sulphuric acid decreases the velocity from $13 \times 10^{-5}$ to $11 \times 10^{-5}$, and $0 \cdot 002M$ reduces it to $8 \times 10^{-5}$ cm./volt sec. Bases have a similar action, and in one case with ammonia the velocity was reduced from $19 \times 10^{-5}$ to $13 \times 10^{-5}$ cm./volt sec. Acids and bases change the colour of colloidal carbon, but the original colour may be regained by neutralisation. In the case of salts, only those of aluminium have any action on the velocity of migration, and in this case the velocity increases to a maximum with $1/500000M$-aluminium sulphate and then falls with greater concentrations. The addition of colloidal ferric hydroxide generally coagulates the colloidal carbon, but if so much colloidal ferric hydroxide is added that no coagulation takes place, then the velocity is reduced about 20%. Dyes, such as crystal-violet, auramine, and methylene-blue, in small concentrations, reduce the velocity to zero and with increasing concentrations then increase it. J. F. S.

**Ionic Synergism. II. Investigation of Mastic Sols.** L. MICHAELIS and N. HIRABAYASHI (*Kolloid Z.*, 1922, **30**, 209—215; cf. A., 1921, ii, 682).—The limiting concentrations of hydrochloric, acetic, sulphuric, nitric, and sulphosalicylic acids, by which precipitation of mastic sols may be brought about, have been determined and the $P_H$ value of the solutions has been measured. The effect of adding lithium chloride, rubidium chloride, sodium carbonate, sodium citrate, calcium chloride, sodium chloride, and potassium sulphate to mastic sols in the presence of measured concentrations of hydrogen-ions has also been investigated. The results show that the anion is not entirely without influence on the precipitation of electro-negative mastic sols; certain anions (sulphosalicylic acid) are strongly antagonistic to the kations, but

the more common anions have so small a specific action that as a first approximation they may be neglected in the investigation of the synergism of the hydrogen-ion and the metallic kations. The results therefore furnish an approximate confirmation of the rules established in the case of congo-rubin (*loc. cit.*) both for the univalent alkali-ions and for the bivalent calcium-ion. From the results, it follows that the relationship of the activity of a uni- and a bi-valent ion cannot be given in absolute terms, but only with reference to the $P_H$ value, and only with increasing value of $P_H$ does the relationship approach an absolute limiting value. Changes in the concentration of the hydrogen- and hydroxyl-ions are only without effect on the condition of a mastic sol when $P_H$ is greater than about seven or eight. J. F. S.

**Soaps and Proteins. I. Colloidal Chemistry of Soaps and the Manufacture of Soap.** MARTIN H. FISCHER, GEORGE D. MCLAUGHLIN, and MARIAN O. HOOKER (*Koll. Chem. Beihefte*, 1922, **15**, 3—102).—A general account of the preparation of soaps, and a consideration, with experimental results of the systems soap–water, soap–alcohol and soap–*X*, where *X* is one of a long series of organic liquids. Definitions of a number of terms in their colloid-chemical significance are given; these include hysteresis, swelling, liquefaction, power of gelatinisation, and solvation, syneresis, and sol. The behaviour of soaps towards indicators and many other properties of soaps are considered. Reproductions of twenty-nine photographs are included in the paper, illustrating the behaviour and properties treated. J. F. S.

**Non-, Uni-, and Bi-variant Equilibria. XXI.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1151—1160; cf. A., 1920, ii, 361).—A theoretical paper in which the author considers the equilibria of *n* components in *n* phases, where the quantity of one of the phases approaches zero. The influence of a new substance on an invariant *P* or *T* equilibrium is discussed. J. F. S.

**Heterogeneous Equilibria: The Ternary System Sodium Sulphate–Sodium Carbonate–Water.** ALFRED ERNEST DAWKINS (T., 1922, **122**, 776—781).

**Nature of Secondary Valency. V. Partition Coefficients in Systems containing Water as one Component, with Special Reference to the Absolute Values of the Series Constants.** HOMER W. SMITH (*J. Physical Chem.*, 1922, **26**, 256—271; cf. this vol., ii, 270).—A continuation of previous work in which the series constants of the partition of organic acids and bases between water and various organic liquids have been derived from data largely taken from the literature. It is shown that in each of these systems the series constants for the various dissolved substances are related to each other in a simple proportion. The series constants for twelve systems in which water is one component have been tentatively formulated by the study of diethylamine. In all twenty of the systems studied, the series constants

for the various systems are related to each other in simple proportion. In every system in which water is one component, the amines differ from the acids in the value of their series constants by a constant amount. It is concluded that the intermolecular forces concerned in the solvent powers of various molecular species differ in intensity by discrete and simply-related amounts.

J. F. S.

**Nature of Secondary Valency. VI.** HOMER W. SMITH (*J. Physical Chem.*, 1922, **26**, 349—357; cf. A., 1921, i, 324; ii, 315; this vol., ii, 270).—The results of the preceding papers are summarised and discussed. It is shown from the examination of twelve hundred determinations of the partition coefficient in twenty-one systems of two immiscible liquids that all may be covered by an equation of the form $100P = V_m/60{\cdot}00 \pm a$, where $V_m$ is the molecular volume at the boiling point and $a$ is a constant. It is found that a limited number of values of $a$ are required to cover the behaviour of all substances in any one system. All substances covered by any one value of $a$ in any system have been termed a series, and the value of $a$ a series constant. The various values of $a$ in any one system are related to one another in simple proportion.

J. F. S.

**Kinetics of Reactions in Heterogeneous Solutions. The Reduction and Oxidation Actions of Alternating Currents.** OSCAR COLLENBERG and SVEN BODFORSS (*Z. physikal. Chem.*, 1922, **101**, 117—149).—The action of metallic iron, copper, zinc, tin, and cadmium on a 4% solution of ferric alum has been investigated by studying the rate of solution of the metals. The results show that the solution of the metals takes place in accordance with Nernst's hypothesis, and the velocity of solution is in keeping with the laws of unimolecular reactions in heterogeneous systems. Apart from zinc, the reaction constant for the individual metals, despite their electrochemical dissimilarity, are very similar. The similarity becomes more apparent when the quantities of the metals dissolved in a given time are compared in terms of equivalents. Using the above metals as electrodes, the electrolysis of ferric alum has been carried out by means of alternating currents of various periodicity; it is shown that the current brings about no fundamental difference in the course of the reaction beyond an increase in the total yield. The influence of the periodicity is very small.

J. F. S.

**Thermal Dissociation of Ammonia with Special Reference to Coke Oven Conditions.** G. E. FOXWELL (*J. Soc. Chem. Ind.*, 1922, **41**T, 114—125).—The thermal decomposition of ammonia diluted with coal gas in silica tubes packed with porous material such as coke or firebrick has been investigated at temperatures between 520° and 850°. It is shown that when an excess solid surface is present the decomposition is bimolecular. The velocity of decomposition, when the tube is filled with coke, increases slowly with increasing temperature, the temperature coefficient being

1·136. The value of the velocity constant, $k$, may be expresse by the Arrhenius formula $k_2=k_1e^{[A(1/T_1-1/T_2)]}$, where $A$ is 13300 For tubes with a radius less than 0·5 cm., $k \propto 1/r^2$, but it is probabl that for wider tubes $k \propto 1/r$. When gases containing ammoni are passed through porous material, the amount of decompositio in unit time varies directly as the square of the radius of the pores hence it is the size of the pores rather than the total porosity tha is of importance. Silica bricks have considerably less decom posing effect than siliceous (80% $SiO_2$) bricks, whilst the presence of iron is very deleterious. The composition of the ash of the coke has an important bearing on the rate of decomposition. Rutile and orthoclase have very little, if any, action; iron pyrites is converted into ferrous sulphide during carbonisation, and this increases the velocity of decomposition to some extent. Iron oxide, which is converted into metallic iron, enormously increases the rate of decomposition and the same is true, although to a less extent, of lime. The value of $k$ for coke is found to be 0·00200 at 755°. J. F. S.

**Decomposition of Nitrous Acid.** ALFONS KLEMENC and FRIEDRICH POLLAK (*Z. physikal. Chem.*, 1922, **101**, 150—171).—The velocity of decomposition of nitrous acid in dilute acid solutions (acetic, nitric, sulphuric) has been determined. The reaction mixture was stirred continuously by a stream of nitrogen to remove the nitric oxide from the solution. It is shown that the velocity of decomposition, according to the equation $3HNO_2=HNO_3+2NO+H_2O$, as measured by the decreasing permanganate titre, depends on the velocity with which the nitric oxide is removed from the solution. This process is determinative of the velocity. The velocity also depends on the pressure of nitric oxide above the solution. It is assumed that undissociated nitrous acid possesses a considerable pressure of nitric oxide and in consequence the velocity of decomposition is proportional to the concentration of undissociated nitrous acid. This fact has been confirmed under the most widely varying conditions. On the basis of the "invasion" and "evasion" coefficients for carbonic acid measured by Bohr, it has been shown that the concentration of free nitric oxide in aqueous solution may be regarded as approximately the same as that of the undissociated nitrous acid. When nitrogen is led through a solution of nitrous acid the velocity of decomposition is increased, and the velocity constant increases with the increasing velocity at which the nitrogen is passed through. The velocity of the direct decomposition of nitrous acid cannot be determined by the method adopted, and is in all probability immeasurably rapid. Nitrous acid decomposes spontaneously into nitric oxide and the hydroxyl radicle and its transitory existence in aqueous solution is due to a mutual action between it and the solvent. The temperature coefficient of the reaction is in keeping with the quantities which define the solubility of a gas. The presence of mineral acids increases the velocity of decomposition. J. F. S.

**Thermal Decomposition of Nitrogen Pentoxide in Solution.** Roger H. Lueck (*J. Amer. Chem. Soc.*, 1922, **44**, 757—769).—The velocity of decomposition of nitrogen pentoxide in carbon tetrachloride and in chloroform solutions has been determined gasometrically at temperatures between 25° and 55°. It is shown that such systems are of special value in considering the newer hypotheses concerning the relationships of radiant energy to chemical action. The fact that the velocity constants obtained in solution so closely approximate to those obtained in the gas phase by Daniels and Johnston (A., 1921, ii, 249) is of particular importance because of the wide variation of conditions under which the measurement has been made. The experimental facts show the energy of activation or the critical increment to be practically independent of the temperature. It has also been shown that, in accordance with a necessary deduction from the Perrin-Lewis radiation theory, a change in reaction velocity brought about by temperature effects or the influence of solvent diminishes as the magnitude of the velocity constant increases. A comparison has been made between the values of the velocity constant experimentally obtained and those calculated from the critical increment, by means of the equation recently put forward by Dushman (A., 1921, ii, 315), and although the agreement is not exact, it is far better than can be obtained by means of tbe older equations developed by Trautz and Lewis. The nitrogen peroxide formed in the reaction has been shown to exert an autocatalytic effect on the thermal decomposition of the nitrogen pentoxide.

J. F. S.

**The Velocity of Absorption of Carbon Dioxide by Alkaline Solutions.** Paul Riou (*Compt. rend.*, 1922, **174**, 1017—1019).—A study of the absorption of carbon dioxide by solutions of sodium carbonate. For a given area of absorbing surface the velocity of absorption of carbon dioxide diminishes as the concentration of the sodium carbonate increases. It is also diminished by the presence of increasing amounts of sodium chloride or hydrogen carbonate. The velocity of absorption is markedly increased by agitation or rise in temperature of the liquid. It is diminished by diluting the carbon dioxide with air.

W. G.

**The Speed of Sulphonation of Phenols. I. The Effect of Temperature and the Methyl Group.** Arthur Fred Campbell (T., 1922, **121**, 847—857).

**Formation and Hydrolysis of Lactones. II.** Anton Kailan and Emanuel Franz Neumann (*Z. physikal. Chem.*, 1922, **101**, 63—93; cf. A., 1920, ii, 606).—The velocity of lactone formation in aqueous and ethyl-alcoholic solutions in the case of hydroxybutyric acid and hydroxyvaleric acid has been determined both in the absence of catalysts and in the presence of hydrochloric, hydriodic, sulphuric, chloroacetic, and *n*-butyric acids. All experiments were carried out at 25°, and in some cases an addition of potassium chloride or sodium chloroacetate was made to the

reaction mixtures. The rate of hydrolysis of butyrolactone anc valerolactone in the presence of hydrochloric acid has also beer determined. It is shown that the autocatalysis of the lacton formation in aqueous solution is practically proportional to th hydrogen-ion concentration alone, and that consequently th results of Henry (A., 1892, ii, 1303), which differ from this result must be attributed to the presence of the silver salt of the hydroxy acid in his solutions. Lactone formation in the presence of chloro acetic acid also depends on the concentration of the hydrogen-ion When hydrochloric acid is used as catalyst in concentrations u to $N/5$, the velocity of lactone formation is proportional to th total concentration of this acid, and if the view be held that th undissociated hydrochloric acid exerts a specific catalytic action then in this case it must be the same as that of the hydrogen-io ($k_m = k_H$). With larger concentrations of hydrochloric acid, th velocity of reaction increases much more rapidly than the hydrogen ion concentration, but more slowly than the total acid concentra tion, so that in these concentrations the action of the undissociatec hydrochloric acid molecule must be decidedly less than that o the hydrogen-ion. This difficulty is removed if the hydrogen-ioi is regarded as the only independent catalyst in this reaction, anc the divergences from the proportionality between concentratior and velocity as due to an increase in the activity of the hydrogen ion brought about by the addition of hydrochloric acid exactly as is the case on the addition of neutral salts. The increase in the velocity of reaction which occurs on the addition of potassium chloride to hydrochloric acid is not to be attributed to a driving back of the dissociation alone, as was assumed by Taylor anc Close (A., 1917, ii, 253), and consequently the deduction of th ratio $k_m/k_H$ from this is not permissible. No connexion could be found between the velocity of reaction and Noyes's activity con stants. The velocity of lactone formation in 99% alcohol, by volume, in the case of γ-hydroxyvaleric acid, both in the presence and absence of hydrochloric acid or other catalysts, takes place much more rapidly than in water. Water exerts a greater retard ation on the velocity of lactone formation by hydrochloric acic than it does in the case of esterification by the same acid. The gradual addition of water causes the velocity of lactone formatior to fall gradually to a point below that obtained in pure water after which it gradually rises to that obtained in pure water. In the autocatalytic lactone formation in 99% alcohol, only a part of the observed velocity is to be explained by the concentration of the hydrogen-ions. J. F. S.

**The Alkaline Hydrolysis of the Esters of the Two Ethylene-dicarboxylic Acids.** ANTON SKRABAL and EMMY RAITH (*Monatsh.*, 1921, **42**, 245—249).—The study of the hydrolysis of ι-tartaric esters (A., 1920, ii, 239) and succinic esters and their wıumologues (A., 1921, ii, 34) has been extended to the investigation presthe alkaline hydrolysis of the methyl esters of fumaric and ˋc acids. The experiments were conducted at 25° in aqueous

solution containing a molecular proportion each of sodium carbonate and sodium hydrogen carbonate, the dilution being necessarily high on account of the low solubility in water of both esters. Referred to $[OH']=1$, the constants for the two stages of the hydrolysis are, for the fumaric ester, $k_1=414$, $k_2=19$, ratio $n=22$; for the maleic ester, $k_1=48$, $k_2=0{\cdot}72$, $n=67$. Comparing these values with the first and second dissociation constants of the acids, which are: fumaric acid $1{\cdot}0\times10^{-3}$ and $3{\cdot}2\times10^{-5}$; maleic acid, $1{\cdot}4\times10^{-2}$ and $2{\cdot}6\times10^{-7}$, fumaric acid falls into line with the saturated, straight chain dicarboxylic acids in that the acid strength and rate of hydrolysis of the esters are symbatic. Maleic acid, however, is abnormal, the first hydrolysis constant being unexpectedly low compared with the high value of the first dissociation constant. The observation may have an important bearing on the question whether there may not be a structural as well as a spatial difference between the two acids. E. H. R.

**Kinetics of the Reaction between Ammonia and Aromatic Aldehydes.** FRIEDRICH DOBLER (*Z. physikal. Chem.*, 1922, **101**, 1—33).—The velocity of the reaction between ammonia and alcoholic solutions of benzaldehyde, *p*-tolualdehyde, *m*-xylylaldehyde, anisaldehyde, cinnamaldehyde, *p*-chlorobenzaldehyde, and *o*-, *m*-, and *p*-nitrobenzaldehydes has been investigated. The method of investigation depends on the fact that ammonia may be estimated in the presence of hydrobenzamide by titration with hydrochloric acid, using hæmatoxylin as indicator. The formation of hydrobenzamide at 20° is shown to be strictly bimolecular, and the corresponding hydramides formed from the other aldehydes are also in most cases formed according to the bimolecular formula. In the case of benzaldehyde and *p*-tolualdehyde, the dependence of the velocity constant on temperature has been determined; it is found that $k$ is nearly doubled by raising the temperature 10° and trebled by raising the temperature 20°, thus: for benzaldehyde, $k_{20°}=0{\cdot}233$, $k_{30°}=0{\cdot}400$ and $k_{40°}=0{\cdot}627$, the two latter values are not very constant. It is found that, on the one hand, an equilibrium is set up between aldehyde and ammonia, and, on the other, between hydramide and water. The influence of temperature on the equilibrium has been investigated, and it is shown that with increasing temperature the equilibrium is displaced so that less hydramide is formed; thus in the case of benzaldehyde at 20°, 48·4% of the ammonia has been converted into hydramide, at 30°, 43·8%; 40°, 36·3% and 50°, 23·2%. An addition of 0·01*N*-benzoic acid practically doubles the reaction velocity in the case of benzaldehyde; small additions of ammonium chloride effect a large increase in the velocity of hydramide formation, in one case this amounted to an increase in the $k$ value from 0·233 to 2·325. Ammonium sulphate has no effect on the specific reaction velocity, whilst sodium hydroxide reduces the $k$ value from 0·233 to 0·028. These changes in velocity are shown to be due to the same cause, namely, changes in the dissociation of ammonium hydroxide. A decrease in the hydroxyl-ion con-

centration increases the specific reaction velocity, and an increase decreases the velocity. Double bonds and chlorine in the para-position in the nucleus of the aldehyde increase the reaction velocity respectively six and three times. The introduction of a methyl group in the para-position, for example, *p*-tolualdehyde, increases the velocity, whilst a second methyl group in the ortho-position, *m*-xylylaldehyde, reduces the value somewhat, but it is still greater than that of the original benzaldehyde. The methoxyl group in anisaldehyde reduces the velocity to about one-half. The substitution of a nitro-group in the meta-position increases the velocity, but in the ortho- and para-positions it reduces the velocity, the para-substitution causing the greater reduction. The ionic concentration of the reaction mixtures does not change during the hydramide formation at 0° and 20°, as is shown by the constant value of the electrical conductivity. J. F. S.

**Catalysts and Chemical Equilibrium.** J. CLARENS (*Bull. Soc. chim.*, 1922, [iv], **31**, 299—307).—From a study of the action of glass wool and cupric chloride respectively as catalysts of the reversible reaction $4HCl+O_2 \rightleftharpoons 2H_2O+2Cl_2$, it is shown that the action of the catalyst is different for each of the inverse reactions which determine the equilibrium. In general, it is considered that there is no reason to suppose that a catalyst modifies equally the velocity of two inverse reactions. W. G.

**The Influencing of the Catalysis of Hydrogen Peroxide with Platinum by Röntgen Rays.** ROBERT SCHWARZ and WALTER FRIEDRICH [with H. WUNNERLICH] (*Ber.*, 1922, **55**, [*B*], 1040—1051).—The catalytic decomposition of hydrogen peroxide in the presence of colloidal platinum is retarded by Röntgen rays, the effect being observed when the mixture of the substances is exposed to the radiation or when the platinum sol is treated in this manner separately and added shortly afterwards to the hydrogen peroxide; the latter alone does not undergo an appreciable change under the influence of Röntgen rays. The maximal value of the retardation is 77% (calculated on the percentage of hydrogen peroxide) and the highest values are observed in the sixth and seventh hours of the experiments. The cause of the phenomenon does not appear to lie in coagulation, diminution in the degree of dispersivity, or alteration in the charge of the particles, as is shown by special experiments, and is rendered improbable by the further observation that the illuminated sol recovers its activity completely within about sixteen hours. It appears probable, therefore, that the platinum sol suffers a reversible change at its surface which must be attributed to the presence of water. Since the action of the Röntgen rays is accompanied by an emission of β-rays from the platinum particles which are able to decompose water, it is possible that an oxide of platinum is formed or that hydrogen is adsorbed by the sol. If, however, it is assumed with Haber that the platinum catalysis of hydrogen peroxide is conditioned by the presence of dissolved or combined oxygen in the catalyst, the formation of an oxide would in all probability accelerate the

change. It is therefore more likely that the first stage of the catalysis is delayed because the platinum charged with hydrogen is not immediately able to form the intermediate product, $Pt_xO_y$. The first stage of the action therefore consists in the combustion of the dissolved hydrogen by oxygen derived from the peroxide after which catalysis can take place in the sense of Haber's theory. The recovery of the platinum sol within sixteen hours is attributed to the gradual decomposition of the platinum hydrogen alloy, and this hypothesis is supported by the known complete instability of the product at 100°. It is also possible that the removal of hydrogen is effected by dissolved atmospheric oxygen, but direct experiments in the absence of oxygen do not lend support to this view, although their interpretation is hampered by the extreme difficulty of excluding oxygen completely in such observations. Pure water is not altered by exposure to Röntgen rays in such a manner as to give rise to contact poisons.

Catalase, also, is altered in such a manner by Röntgen rays that its power to catalyse the decomposition of hydrogen peroxide is lessened; as with the platinum sol, the enzyme recovers its activity completely after several hours. A satisfactory explanation of the phenomena cannot yet be given. H. W.

**The Catalytic Activity of Copper.** W. G. PALMER (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 175—186; cf. A., 1920, ii, 609; 1921, ii, 542).—This communication describes the effect on the dehydrogenating activity of copper of the addition of magnesium oxide, ferric oxide, zinc oxide, manganous oxide, and sodium carbonate. The presence of small amounts of sodium carbonate completely destroys the activity. The addition of 1% or less of an oxide reduces the activity considerably, but with higher concentrations, owing to the separation of two phases, an increase in the catalytic effect is observed. The pure oxides are usually less active than pure copper, and hence must be deficient in the density of radiation of about 1·0 $\mu$ wave-length (cf. previous papers). They, however, adsorb water and probably alcohol to a greater extent than metals, but this increase may be counteracted by the opacity of the oxide film to radiation from the copper core. Increased adsorption thus increases the activity, provided the oxide films are transparent to the radiation of the main catalyst.

W. E. G.

**A Defined Organic Catalyst with a Hydrogen-ion Optimum.** ERIK WIDMARK and CARL ALEX JEPPSSON (*Skand. Arch. Physiol.*, 1922, **42**, 43—61; from *Physiol. Abstr.*, 1922, **7**, 6; cf. A., 1921, i, 183).—The kinetics of the catalysis of acetoacetic acid into acetone and carbon dioxide is investigated in detail. It is found to have a reaction optimum at $P_H$ 4·09, and this corresponds exactly with the optimum reaction calculated on the assumption that only undissociated molecules of catalyst and of substrate enter into the reaction. For this calculation from the dissociation constants, the original must be consulted. The conclusion is drawn that only the undissociated aniline molecule is effective,

and acts only on the undissociated molecule of acetoacetic acid. The conclusion cannot be generalised: for example, alanine has its optimum at $P_H$ 8, at which reaction acetoacetic acid is almost completely ionised. The suggestive comparison with the behaviour of enzymes is indicated. W. O. K.

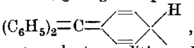
**The Böhr Atom. The Lagrange Theorem applied to Electronic Orbits.** MARCEL BRILLOUIN (*J. Phys. Radium*, 1922, **3**, 65—73).—A mathematical paper emphasising the exclusively spectroscopic character of Böhr's theory. W. E. G.

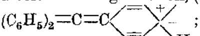
**Atoms and Molecules. II.** ALBERT C. CREHORE (*Phil. Mag.*, [vi], **43**, 886—914; cf. A., 1921, ii, 632).—A theory of the structure of atoms is presented which is in conformity with the Saha form of the electromagnetic theory. In the models given, the negative electron is assumed to be an oblate spheroid with a ratio of axes about three to one and the hydrogen atom consists of a positive charge of two units with very small dimensions situated in between two negative electrons. A structure is suggested for nitrogen and oxygen, which indicates that the heavier products of disintegration found by Rutherford may possess a mass 12 and a charge of 5.

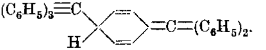
It is also sought to compute the known distances between the atoms forming a molecule. The shape of the negative electron is a most important factor in determining the equilibrium distance, and hence it is a universal distance. Only electrostatic forces are considered, and it is shown that equilibrium is possible between the attractive and repulsive forces of the atoms and electrons when the eccentricity of the electron lies between the limits 0·9 and 1·0. This agrees with the value found in the previous paper. It is shown that helium and neon atoms will not form compounds and must be monatomic. W. E. G.

**Unsymmetrical Addition to the Double Bond. I. A Theory of the Reaction Mechanism of the Direct Union.** GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, **19**, 645—660; cf. this vol., A., ii, 138).—A theory of the mechanism of chemical reaction based on the Langmuir octet theory of valence. Diagrams are given showing the relationships between the forces of attraction and repulsion for two types of reaction, (*a*) a direct addition reaction, where an interpenetration of the outer shells of electrons occurs, and (*b*) a dissociation addition reaction where only secondary valence comes into play. These two types are illustrated by double bond reactions. W. E. G.

**The Dissociation of Hexaphenylethane from the Point of View of the Octet Theory of Valence.** HOWARD IRVING COLE (*Philippine J. Sci.*, 1921, **19**, 681—690).—A historical survey of the previous investigations on the dissociation of hexaphenylethane is given and the Lewis-Langmuir octet theory of valence applied to this problem on the lines suggested by Perkins (this vol., A., ii, 138). On this theory hexaphenylethane cannot possibly dissociate without a rearrangement of one or more of the phenyl

groups. Symmetrical dissociation occurs in non-ionising solvents such as benzene, giving the quinoid modification as in Gomberg's formula,  , which contains a para-carbon atom in a tervalent condition. In an ionising solvent such as sulphur dioxide, which contains unshared electrons, the dissociation occurs unsymmetrically. An unstable union with a solvent molecule takes place, which supplies two electrons to the shell of one of the carbon atoms in a phenyl group. In this manner is obtained a colourless negative ion, $(C_6H_5)_3{\equiv}C^-$, and a coloured positive ion,

 ; the latter *exists only in combination* with a solvent molecule. These two ions can combine to give

 These modifications are essentially the same as those of Gomberg, except that, on this view, colourless triphenylmethyl can exist only in the form of a negative ion. The physical and chemical properties appear to support this theory. The oxidation of triphenylmethyl to form a peroxide is explained by the formation of intermediate positive and negative ions. An oxygen molecule is added to the positively charged ion, which then combines with the negative ion to give the peroxide. W. E. G.

**A Proposed Laboratory Test of the Theory of Relativity.** Harold S. King (*Nature*, 1922, **109**, 582—583).—Since it is impossible to conceive of the annihilation of mass, such as appears in the synthesis of an atom of helium from four hydrogen atoms, it must be supposed that mass is electromagnetic in origin, loss of mass being ascribed to overlapping of fields. According to the theory of relativity, 1 gram of matter is equivalent to $9\times10^{20}$ ergs, or $2{\cdot}1\times10^{13}$ calories; moreover, 1 gram of radium in disintegrating to lead evolves $3{\cdot}7\times10^{9}$ cal. Thus, it is possible to calculate the atomic weight of radium (226·038) by addition of 1 gram atom of radium-*G* (206·000), 5 gram atoms of helium (20·000), 4 gram electrons (0·0005) [?], and $3{\cdot}7\times10^{9}$ cal. (0·038). If Hönigschmid's value (225·97) for the atomic weight of radium is accepted, it would therefore appear that radium-*G* has an atomic weight less than 206 (the lowest experimental figures being 206·08 and 206·05, due respectively to Richards and Hönigschmid), or that energy is derived from outside sources as suggested by Perrin, or that the equation connecting mass and energy is not correct. It is therefore suggested that an extension of the method of positive ray analysis to the determination of the atomic weights of radium, radium-*G*, and helium to an accuracy of 1 part in 10,000 not only would be of intrinsic value, but also would show whether the relation of mass and energy, based on the theory of relativity, holds.

A. A. E.

# Inorganic Chemistry.

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**A Simple Hydrogen Generator for Use in making Hydrogen ion Determinations.** P. H. CATHCART (*J. Ind. Eng. Chem* 1922, **14**, 278).—The hydrogen is generated electrolytically in bell jar inverted in a cylinder containing 10% sodium hydroxide The outer vessel consists of a large glass precipitating jar, th hydrogen reservoir being a large inverted percolator with its mout resting on a support about 1 inch from the bottom of the precipit ating jar. A rubber stopper in the top of the hydrogen reservoi carries the cathode (which consists of an iron disk suspended fror an iron wire) and a glass tube with stop-cock. The inner vessel i held down by four rubber-covered wires. The anode is similar t the cathode, of about 4 sq. in. area, and so adjusted in the annula space between the two vessels that it just touches the liquid whe all gas has been withdrawn from the reservoir. The cathode jus projects below the lower rim of the reservoir. A 110 volt D.C circuit was used for generating the hydrogen, with a switch s arranged that the current is automatically cut off when the reservoi becomes full. A diagram of the apparatus is given. H. C. R.

**Rectilinear Diameter of Hydrogen.** E. MATHIAS, C. A. CROM MELIN, and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch Amsterdam*, 1922, **23**, 1175—1184; cf. A., 1921, ii, 256).—The densit of liquid and gaseous hydrogen has been determined in grams/c.c at temperatures from $-240\cdot57°$ to $-249\cdot89°$. The critical densit is calculated from the results and the value 0·03102 obtained, figure which is considerably smaller than the corresponding figur for any other substance. The equation of the diameter of th form $y=a+bt$ is considered, and the values of the coefficient ar evaluated from the experimental data. The values obtained ar $a=-0\cdot063510$ and $b=-0\cdot00039402$. The value of the slope o the diameter $b$ is the smallest observed for any substance.

J. F. S.

**The Crystal Structure of Ice.** (SIR) W. H. BRAGG (*Proc Physical Soc.*, 1922, **34**, 98—103).—This is derived independentl of direct $X$-ray analysis on certain suppositions connected wit the low density of ice. St. John (*Proc. Nat. Acad. Sci.*, 1918, **4** 193) and Dennison (*Physical Rev.*, 1921, **17**, 20) have applied th methods of $X$-ray analysis and both refer the structure to a lattic composed of four right triangular prisms but disagree as to th dimensions. In the present paper it is assumed that ice belong to that class of crystals in which the molecules are broken up int positive and negative ions, the hydrogens having given up thei valency electrons to the oxygens. The density of ice is so lov that the most economical spacing is adopted; the atoms are arrange a hexagonal lattice with each oxygen surrounded by four hydrogen each hydrogen by two oxygens. The distance between th

entres of two oxygen atoms is 2·76, the distance between consecutive basal planes is 3·67, and the distance between two atoms n the same plane is 4·52. The structure is extremely empty and loose arrangement of water molecules would occupy less space. The hydrogen atom has apparently a larger diameter than the xygen atom if oxygen has the value 1·30. These results agree xactly with the $X$-ray analysis of Dennison and the conclusions re supported by a comparison between the calculated and observed ntensities of reflection. W. E. G.

**The Variations in the Chemical Composition of Sea-water nd the Evaluation of the Saline Content.** GABRIEL BERTRAND, 'REUNDLER, and (MLLE) MÉNAGER (*Compt. rend.*, 1922, **174**, 1251—253).—The authors have determined the total halogens and the alcium and magnesium in the water from the Atlantic ocean and he Mediterranean sea. The halogens being calculated as chlorine, he ratio of chlorine to calcium and magnesium respectively in the wo samples of water was by no means the same. Thus the method f evaluating the saline content of sea-water from the density or hlorine content by means of Knudsen's tables can only be con-.dered as at the best an approximation. W. G.

**The Dissociation of Chlorine.** H. VON WARTENBERG and . A. HENGLEIN (*Ber.*, 1922, **55**, [*B*], 1003—1006).—Difficulties re experienced in attempting to measure the dissociation of active ases such as chlorine hy observation of the abnormal increase of ressure when they are heated owing to the impossibility of finding completely resistant material for the construction of the apparatus. ince, however, the dissociation of binary compounds is dependent n the total pressure, it is possible to effect such measurements at emperatures which silica vessels will withstand if an extremely ow pressure is used. In this manner, preliminary measurements f the dissociation of chlorine at $10^{-3}$ mm. pressure have been made. The apparatus consists of a quartz bulb surrounded by a quartz nantle, the space between the two being continuously evacuated. The bulb is connected with a 2 mm. wide quartz capillary which eads to a quartz thread manometer and mercury seal cooled to -30° and thence to a Volmer pump. The chlorine is generated y heating auric chloride in a glass capillary which is subsequently ealed off. The bulb is surrounded by platinum foil and heated n a Heraeus furnace, the temperature measurements being accurate o ±2°. The temperature interval ranges from 985° to 1151° bsolute.

It is certain that the heat of dissociation of chlorine is considerbly lower than the value 106,000 cal. usually adopted and for $T=0$ is about 70,000 cal. H. W.

**The Structure of Chlorine Dioxide and Related Compounds.** GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, **19**, 29—740; cf. this vol., ii, 138).—A discussion of the constitutional formulæ of some of the oxides of chlorine and nitrogen. n the Langmuir theory no place is given to bonds consisting of

one, three, or five electrons. The suggestion is made that in exceptional cases an odd number of electrons may form a chemical bond. In chlorine dioxide, five electrons are shared between the three atoms as in the formula :

$$:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\dot{Cl}}\vdots\underset{\cdot\cdot}{\dot{O}}:$$

On this view chlorine dioxide contains a three electron bond. An odd electron is also shared in nitric oxide and nitrogen peroxide. The electron binding strength of atoms and its variation with the covalence is discussed. W. E. G.

**Hydroxylamine. I. Simple Method of Preparation of Free Hydroxylamine.** HANS LECHER and JOSEF HOFMANN (*Ber.*, 1922, **55**, [*B*], 912—919).—The method adopted is essentially a modification of that of Lobry de Bruyn, its most important feature being the avoidance of the final distillation of the product.

The apparatus consists of a Brühl receiver in which the reaction vessel is placed. The lower tubulus (generally used for evacuation) is provided with a calcium chloride tube whilst the upper tubulus is fitted with a stopper carrying two dropping funnels, the ends of which are placed above the reaction vessel. The tubulus of the lid serves for the introduction of a very efficient stirrer, which is provided with the customary mercury seal. The finely divided hydroxylamine hydrochloride is suspended in absolute ethyl alcohol in the reaction vessel and a small quantity of solid phenolphthalein is added. A solution of sodium ethoxide in absolute ethyl alcohol is introduced slowly from one of the dropping funnels into the well-stirred suspension, the rate of addition being so controlled that the red coloration which occurs as each drop enters the suspension disappears instantaneously. Should ultimately a pale pink coloration persist, it is removed by cautious addition of a solution of hydroxylamine hydrochloride in ethyl alcohol from the second dropping funnel. The precipitated sodium chloride is removed and the filtrate allowed to remain undisturbed in a freezing mixture of ice and salt until it attains a temperature of $-18°$. The large crystals of hydroxylamine thus produced are filtered, washed with absolute ether, and brought into a desiccator which is immediately exhausted. In this manner, there is no loss of hydroxylamine by decomposition during the preparation, but about 5·4% of it is retained by the precipitated sodium chloride. The yield of solid hydroxylamine is about 40% of that theoretically possible, but the remainder can be readily recovered as the hydrochloride from the alcoholic mother-liquor. The product contains about 97% of hydroxylamine, the remainder being water. It has m. p. 32—35°, $d^{16}$ 1·335, $d^{14}$ 1·334. It is distinguished from Lobry de Bruyn's purest specimens by its greater instability; after twenty-four hours it smells of ammonia and after four days it is completely liquefied and contains only 42·55% of hydroxylamine. Hydroxylamine crystallises in the rhombic system; the crystals obtained from ethyl alcohol and by the solidification of the molten substance are identical. H. W.

**Behaviour of Carbon at High Temperatures.** F. SAUERWALD (*Z. Elektrochem.*, 1922, **28**, 183—185).—Continuing the work of Ryschkewitsch (A., 1921, ii, 258, 586, 696) and Münch (A., 1921, ii, 586), the author heated rods of carbon and graphite to various temperatures, attaining finally the temperature of the positive crater of the arc. The heating was effected by passing a current through the rods in an atmosphere of hydrogen. The ends of the rods were copper-plated. Small globules appeared on the surface of the Acheson graphite employed, and these are attributed to the distillation of impurities from the hotter interior of the rod to the surface. This was confirmed by a determination of the respective ash contents of the rod and of the globules. The conclusion is not in agreement with that of Ryschkewitsch, who found similar globules to be composed of pure graphite. J. S. G. T.

**Behaviour of Carbon at High Temperatures.** EUGEN RYSCHKEWITSCH (*Z. Elektrochem.*, 1922, **28**, 185—186).—The author contends that the experimental conditions employed by Sauerwald (see preceding abstract), differ so materially from his own, that the results obtained in the two cases are not comparable. He remarks more particularly on the different atmospheres and current densities employed in the two cases, and on the possibility of impurities being derived, in Sauerwald's experiments, from the heated metallic connexions employed. J. S. G. T.

**Preferential Catalytic Combustion of Carbon Monoxide in Hydrogen.** ARTHUR B. LAMB, CHARLES C. SCALIONE, and GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1922, **44**, 738—757).—With the object of finding a method of removing small quantities of carbon monoxide from hydrogen before its use in the synthetic production of ammonia, a number of experiments have been carried out on the preferential combustion of carbon monoxide in mixtures containing air, hydrogen, carbon monoxide, and carbon dioxide by means of a catalyst termed "hopcalite," which is a mixture of metallic oxides and in the present experiments was composed of 60% of manganese dioxide and 40% of cupric oxide. It is shown that "hopcalite," which oxidises carbon monoxide in air rapidly and catalytically at the ordinary temperature, does not affect hydrogen in air under the same conditions, and that by its means carbon monoxide can be completely and continuously removed from a dry mixture containing, for example, 0·5% of carbon monoxide, 89·50% of hydrogen, and 10% of air without any noticeable action on the hydrogen. A similar mixture containing 1% of carbon monoxide, on the other hand, liberates so much heat that under these conditions oxidation of the hydrogen sets in, and the catalyst is soon heated to incandescence and is destroyed. It is also shown that moist mixtures of carbon monoxide and air and of hydrogen and air require much higher temperatures for oxidation. In the presence of water vapour at a pressure of 50 mm. of mercury, carbon monoxide in a 0·5% mixture with air is completely oxidised at a temperature of 90° or lower. Hydrogen, on the other hand, mixed with air, does not begin to be oxidised under these conditions

until a temperature of 120—125° is reached. It is possible, therefore, to remove carbon monoxide completely and continuously from a mixture having, for example, the composition 0·5% of carbon monoxide, 0·5% of oxygen, 24·75% of nitrogen, and 74·25% of hydrogen and containing water vapour at a pressure of 50 mm. of mercury without any considerable oxidation of hydrogen. On the other hand, in a similar 1% carbon monoxide mixture, the hydrogen soon takes fire and the catalyst becomes incandescent. The effect of space velocity, carbon dioxide, hydrogen sulphide, and the concentration of carbon monoxide on the efficiency of the catalyst have been investigated. Formulæ for the temperature rise in the catalyst, and the factor limiting the permissible concentration of carbon monoxide have been derived and verified at different space velocities in tubes of various diameters, and on the basis of these results the proper conditions for the technical application of this method of removing carbon monoxide from hydrogen have been outlined. The present results are in agreement with those of Rideal (T., 1919, **115**, 993). J. F. S.

**Preparation of Bright Metallic Sodium and Potassium, or their Alloys, in Nitrogen.** G. BORNEMANN (*Z. angew. Chem.*, 1922, **35**, 227).—A glass tube of 15—20 mm. diameter is drawn out into a short constriction of 3—4 mm. diameter about 20 cm. from one end which is sealed up. A fine wire gauze thimble is fitted tightly into the tube above the constriction and the required amount of metal introduced into the open end of the tube, which is then sealed. The tube is then placed in a horizontal position and the metal melted, whereby the oxygen, moisture, and carbon dioxide are removed, leaving an atmosphere of nitrogen. On now placing the tube vertically and carefully remelting the metal it flows through the gauze and the constriction into the lower portion of the tube as perfectly bright untarnished metal, all impurities remaining behind on the gauze filter. The tube is then drawn off and sealed at the constriction. G. F. M.

**Sodium Silicate.** A. ERDENBRECHER (*Mikrokosmos*, 1921, **15**, 55—60).—The addition of not more than 40 grams of sodium hydroxide to 100 c.c. of the solution obtained when 20—25 grams of the salt $Na_2SiO_3,9—10H_2O$ are dissolved in 40 c.c. of water yields the hydrate $Na_2SiO_3,9H_2O$, rhombic, m. p. 47°. Sixty grams of sodium hydroxide similarly yield the hydrate $Na_2SiO_3,6H_2O$, monoclinic, m. p. 63·5°, whilst larger amounts yield the hydrate $Na_2SiO_3,4H_2O$, hexagonal, m. p. 83—85°. Other hydrates of sodium metasilicate mentioned in the literature are probably mixtures of these, as changes in the composition of the mother-liquor cause changes in the degree of hydration.

CHEMICAL ABSTRACTS.

**Preparation of Ammonium Chloride.** P. MONDAIN MONVAL (*Compt. rend.*, 1922, **174**, 1014—1017).—A study of the conditions governing the crystallisation of ammonium chloride from solution at 15° when in solution alone or in the presence of one or more of

the salts, sodium chloride, sodium carbonate, and ammonium carbonate. A Le Chatelier diagram showing the surfaces of saturation is given. Commercially in the ammonia-soda process the salt is not crystallised out from the liquid from which the sodium hydrogen carbonate has been extracted, but ammonia is first added to convert the hydrogen carbonates into normal carbonates. W. G.

**The Melting Point of Normal Ammonium Sulphate.** R. KATTWINKEL (*Ber.*, 1922, **55**, [*B*], 874).—Contrary to the statement of Caspar (A., 1920, ii, 431), a definite melting point cannot be assigned to normal ammonium sulphate; with increasing temperature it suffers loss of ammonia, decomposition being complete at 365°. H. W.

**Conditions of Formation and Stability of Ammonium Carbamate.** C. MATIGNON and M. FRÉJACQUES (*Bull. Soc. chim.*, 1922, [iv], **31**, 307—316).—A more detailed account of work already published (A., 1920, ii, 250). W. G.

**Liquid Crystals of Calcium Phosphate.** P. GAUBERT (*Compt. rend.*, 1922, **174**, 1115—1117).—When the rhombohedra obtained by crushing calcite are ignited, they retain their shape and if then they are submitted to the action of phosphoric acid certain optical phenomena are observed due to the formation of liquid or soft crystals of calcium phosphate. These are described in detail. W. G.

**Action of Nitrogen on Mixtures of Barium Oxide and Carbon at High Temperatures.** PAUL ASKENASY and FRITHJOF GRUDE (*Z. Elektrochem.*, 1922, **28**, 130—151).—The rate of combination of compressed mixtures of barium carbonate and wood charcoal or graphite with nitrogen has been investigated up to 1600°. It is shown that the reaction proceeds with a practicable velocity at 1400°, and in fifteen minutes 60% of the barium has been converted into a mixture of cyanide and cyanamide when an excess of nitrogen is present. In agreement with Caro and in opposition to Ewan and Napier, the primary reaction is the formation of barium carbide, and from this much cyanide is formed which then undergoes a secondary reaction to form barium cyanamide. The formation of cyanide at comparatively low temperatures (1300—1400°) reaches a maximum of 65% in fifteen to thirty minutes, which is not increased at 1600°. With increasing temperature, the formation of the cyanamide rapidly increases. There is no evidence that a basic cyanide is first formed, nor is there any evidence of a sublimation of barium cyanide at the lower temperatures. The reproducibility of the combination of nitrogen is best achieved in the presence of an excess of carbon. When there is a shortage of carbon it is the cyanamide formation, and not that of the cyanide, which is effected. It is shown that the reaction proceeds more rapidly when compressed materials are used. Impurities in the carbon, such as silica or alumina, retard the reaction, whilst iron, in opposition to previous statements, accelerates it, but disturbs the reproducibility. A mixture of barium oxide and carbon takes up the same amount of

nitrogen as an equivalent quantity of 55% barium carbide, and the relative amounts of barium cyanide and cyanamide formed are the same in both cases. A very long list of references on this subject, with comments, precedes the paper. J. F. S.

**Electro-deposition of Lead from Mathers's Perchlorate Bath. I. Structure of the Deposit.** W. E. HUGHES (*J. Physical Chem.*, 1922, **26**, 316—323).—The author has made a macroscopic and microscopic examination of the structure of lead deposited from Mathers's perchlorate bath (U.S. Pat. 931944, 1909; A., 1911, ii, 113). The specimens were etched by using them as anodes in the electrolysis of 30 c.c. of 30% perchloric acid in 270 c.c. of water for various periods with a current density of 9—10 amperes/sq. dcm. and a voltage of 1·5. The etched surface was much worn, cindery, and dull and light grey in colour with no crystalline appearance. Where the outside surface of the lead was directed toward the cathode during etching, a thin, skin-like substance is formed, which after a while detaches itself and comes away in flakes; no such action occurs when the inside surface is directed to the cathode. The term inside surface indicates the lead surface which was in contact with the cathode during the deposition. When examined microscopically (125 diameters) the deposit is seen to consist of irregular cells with lustrous, slightly yellow walls. The interior of each cell appeared to be made up of a mosaic of small bright and dark particles. The author deduces from the observations that the structure of the lead is ordered, and not amorphous; the size of the grain is reduced by the colloid (peptone) contained in the bath and that the colloid separates from solution with the lead, not in any haphazard fashion, but in continuous layers in the deposit. J. F. S.

**Amalgams. III. Colloidal Copper Amalgam.** C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 215—228; cf. A., 1919, ii, 69, 516).—Hydrosols of copper amalgam may be prepared by (*a*) shaking copper hydrosol with mercury, (*b*) keeping copper hydrosol in contact with mercury without shaking, (*c*) mixing either red or blue copper hydrosol with mercury hydrosol. The preparations were all effected in an atmosphere of hydrogen, and the amalgam sols possess colours which differ markedly from those of the original copper sols. In the first preparation, sols of an amalgam represented by the formula $CuHg_{0\cdot02}$ may be obtained, in the second preparation the composition of the amalgam is given by the formula $CuHg_{0\cdot34}$, and in the third preparation, using the red copper hydrosol, the amalgam has the composition $CuHg_{1\cdot35}$. The copper amalgam sols are less stable and more easily oxidised than the gold amalgam hydrosols previously described (*loc. cit.*), and require a larger concentration of protecting colloid (sodium lysalbate or sodium protalbate) to stabilise them than the corresponding gold amalgam sols. J. F. S.

**Copper Sulphide.** W. GLUUD (*Ber.*, 1922, **55**, [*B*], 952—953).—The oxidation of copper sulphide by air at the atmospheric

pressure proceeds rapidly in ammoniacal suspension with the production of a mixture of sulphate and thiosulphate; cuprous sulphide is similarly but more slowly oxidised. In neutral or acid solution, the change is slower and necessitates the use of compressed air at temperatures up to 160°; copper sulphate is formed. In certain circumstances the sulphur is deposited in the elementary state; the chief conditions are that the copper solution should not be precipitated completely, that the oxidation should be effected immediately, and that the solution should contain, in addition to ammonia, considerable amounts of dissolved salts, preferably ammonium compounds. H. W.

**Mechanism of the Dehydration of Crystalline Aluminium Hydroxide and of the Adsorption of Water by the Resulting Alumina.** LOWELL H. MILLIGAN (*J. Physical Chem.*, 1922, **26**, 247—255).—Crystalline aluminium hydroxide in air at atmospheric pressure and humidity is not affected by temperatures below 145°, and remains constant in composition as the normal hydroxide, $Al(OH)_3$, up to this temperature. The decomposition and evolution of water commences just above 145°, and as far as the evolution of the chemically combined water of the hydroxide is concerned, is practically complete at 200°. Slight irregularities are observed in the drying curve between 145° and 196°, which are attributed to the very slow rate at which equilibrium is reached at these particular temperatures and the resultant experimental errors. All the water is not driven off at 200°, but an amount equal to about 8% of the original aluminium hydroxide is retained at this temperature, and is driven off slowly as the ignition temperature is increased, very much higher temperatures being required for complete dehydration. Above 200°, the curve has the general form of an adsorption curve, and the 8% of water, which is retained at 200°, appears to be practically adsorbed by the highly porous aluminium oxide. There is no evidence of the existence of hydrates formed by step-wise dehydration. When alumina, produced by drying aluminium hydroxide at temperatures as low as 275°, is allowed to take up water, this water is simply adsorbed, and does not recombine chemically with the alumina. This is established by the fact that the drying curve after "rehydration" bears no resemblance to the original dehydration curve of aluminium hydroxide. The higher the ignition temperature at which alumina is prepared the smaller is the amount of water which it is capable of adsorbing under a given set of conditions.

[With W. J. MEAD.]—The original aluminium hydroxide, the alumina prepared by its ignition, and the alumina after "rehydration" have been subjected to an *X*-ray examination. It is shown that the *X*-ray pattern produced by the original crystalline aluminium hydroxide is identical with that of the mineral gibbsite, which is a definitely crystalline chemical compound. Alumina prepared by calcining the crystalline hydroxide at 325° gives no trace of the hydroxide structure, neither is it similar to the mineral diaspore, $Al_2O_3,H_2O$, nor to corundum, $Al_2O_3$. It shows a set of

lines which indicate a crystalline structure. The adsorption of water does not alter its structure. Alumina prepared by calcination at 600° shows a faint pattern similar to the preceding specimen, but the bulk of the material is probably amorphous. When calcination temperatures somewhat above 1000° are employed, the product gives a faint corundum pattern, and still higher temperatures increase the intensity of this pattern until it becomes that of pure corundum. J. F. S.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. I. Reaction between [Potassium] Permanganate and Formic Acid in Slightly Acid Solution.** JOSEF HOLLUTA (*Z. physikal. Chem.*, 1922, **101**, 34—53).—The velocity of the reduction of potassium permanganate by formic acid in faintly acid solutions has been investigated at 22°, 25·1°, 24·7°, and 15·3°. The results are discussed in connexion with previously published work of Schilov (A., 1903, ii, 720) and of Skrabal (A., 1905, ii, 17, 18; 1906, ii, 658), and it is shown that the reduction takes place in the following stages: (1) $2(MnO_4'+HCO_2'=MnO_4'''+H^{\cdot}+CO_2)$ (measurably slow); (2) $2MnO_4'''+8H^{\cdot}+5HCO_2'=MnO_4'+Mn(HCO_2)_5''+4H_2O$ (instantaneous); (3) $Mn(HCO_2)_5''=Mn^{\cdot\cdot\cdot}+5HCO_2'$ (equilibrium); (4) $2Mn^{\cdot\cdot\cdot}+HCO_2'=2Mn^{\cdot\cdot}+H^{\cdot}+CO_2$ (more rapid than 1); (5) $2(2Mn^{\cdot\cdot\cdot}+4H_2O=Mn^{\cdot\cdot}+Mn(OH)_4+4H^{\cdot})$ (immeasurably fast); (6) $MnO_4'+4Mn^{\cdot\cdot}+8H^{\cdot}=5Mn^{\cdot\cdot\cdot}+4H_2O$ (immeasurably fast); (7) $2(Mn[OH]_4+4H^{\cdot}=Mn^{\cdot\cdot\cdot\cdot}+4H_2O)$ (equilibrium), and (8) $2Mn^{\cdot\cdot\cdot\cdot}+HCO_2'=Mn^{\cdot\cdot}+H^{\cdot}+CO_2$ (very slow). These partial equations give a total equation for the reaction which has the form $2MnO_4'+11H^{\cdot}+5HCO_2'=2Mn^{\cdot\cdot}+5CO_2+8H_2O$. The measured temperature coefficient for 10° is 1·86. J. F. S.

**Mixed Crystal Formation in Ternary Systems containing Water, Ammonium Chloride, and Ferrous, Cobaltous, or Nickel Chloride.** FREDERICK WILLIAM JEFFREY CLENDINNEN (T., 1922, **121**, 801—805).

**Complex Nitrites of Nickel.** V. CUTTICA (*Gazzetta*, 1922, **52**, i, 210—215).—In consequence of the slight tendency to dissociate exhibited by nickel nitrite, the latter is able to form complexes, double nickel nitrites occupying a position between true complex compounds and double salts and possessing the constant co-ordination number of the former and the great mobility of the component simple ions in solution shown by the latter. Cryoscopic measurements of aqueous solutions of nickel thallium nitrite, $4TlNO_2,Ni(NO_2)_2$, give a molecular weight of 107—111, the calculated value being 1050; hence rather more than nine of the eleven simple ions are manifest in solution. Since thallium nitrite is completely dissociated in the experimental conditions employed, the nickel nitrite is only partly dissociated.

Owing to the markedly "imperfect" nature of double nickel nitrites it is necessary, in the preparation of triple nickel nitrites, that the active masses of the component ions be high in order

that undissociated molecules of the complex may be formed and that the solubility product may be exceeded. The failure of Przibylla (A., 1898, ii, 162; 1899, ii, 222) and of Reichard (A., 1904, ii, 488, 741) to obtain triple nickel cadmium nitrites was probably due to neglect of this condition. The author has prepared *nickel cadmium potassium nitrite*, $Ni(NO_2)_2,2Cd(NO_2)_2,4KNO_2$, which is pale yellow; *nickel cadmium thallium nitrite*, of analogous formula, which is brick red, and *nickel cadmium ammonium nitrite*, $Ni(NO_2)_2,Cd(NO_2)_2,2NH_4NO_2$, which is pale flesh-coloured. These three compounds are profoundly disgregated by the dissociating action of water, the nickel and cadmium nitrites undergoing only limited dissociation.

Many of the triple nickel nitrites known may be represented by the general scheme for the double nickel nitrites, for example, $\left[Ni(NO_2)_6\right]^{Ba(Ca,Sr,Pb)}_{K_2}$, $\left[Ni(NO_2)_6\right]^{Cd}_{(NH_4)_2}$, the nickel in these exhibiting analogy to iron and cobalt. In the case of nickel cadmium potassium and nickel cadmium thallium nitrites, which do not correspond with this scheme, if the fundamental co-ordinating action capable of functioning in two concentric spheres is attributed to the nickel, it may be assumed that in the inner sphere are co-ordinated six nitrous residues in the same ion as occurs in the other nickel nitrites and that in the second sphere two whole cadmium nitrite molecules remain bound. This supposition, expressed by the formula $\left[Ni(NO_2)_6\right]^{K(Tl)_4}_{[Cd(NO_2)_2]_2}$, is in accord with the similarity in colour between these compounds and the double and certain other triple nickel nitrites. T. H. P.

**Complex Chlorides containing Gold. I. Pollard's Ammonium Silver Auric Chloride.** Horace L. Wells (*Amer. J. Sci.*, 1922, **3**, [v], (16), 257—259).—The triple chloride examined by Pollard (T., 1920, **117**, 99) was investigated. It was found that when solutions somewhat similar to the one recommended by Pollard were diluted with an equal volume or more of 1 : 1, or stronger, hydrochloric acid better products for analysis were obtained. The results of analysis suggest the formula $(NH_4)_6Ag_2Au_3Cl_{17}$ for the triple salt against $(NH_4)_8Ag_3Au_4Cl_{23}$ put forward by Pollard. The corresponding potassium salt could not be obtained, but a triple salt of cæsium was prepared and is being investigated. W. T.

**Complex Chlorides containing Gold. II. Cæsium Triple Salts.** Horace L. Wells (*Amer. J. Sci.*, 1922, **3**, [v], 315—326).—Five new triple chlorides of cæsium have been prepared. $Cs_4Ag_2Au'''_2Cl_{12}$, very black, opaque, powder black. $Cs_4ZnAu'''_2Cl_{12}$, yellow (sometimes red), transparent, powder pale yellow. $Cs_4HgAu'''_2Cl_{12}$, orange, transparent, powder yellow. $Cs_4CuAu'''_2Cl_{12}$, crystals black, powder pale brown. $Cs_4Au_2'Au'''_2Cl_{12}$, very black, opaque, powder black. These triple salts are apparently isomorphous, an interesting case of isomorphous replacement of two univalent atoms by one bivalent atom. Cæsium calcium auric

chloride could not be prepared. These cæsium triple salts do not correspond with the ammonium triple chloride (Wells, preceding abstract). In preparing these triple chlorides a large excess of cæsium chloride over the theoretical quantity is desirable, but the solutions should be very dilute in respect to gold in order to avoid the deposition of the sparingly soluble cæsium auric chloride. Presence of concentrated hydrochloric acid is favourable. W. T.

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## Mineralogical Chemistry.

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**Cristobalite in Basalt from Washington.** Earl V. Shannon (*J. Washington Acad. Sci.*, 1922, **12**, 195—196).—Minute, white crystals of cristobalite ($SiO_2$) occur with plagioclase, magnetite, opal, etc., in the steam-cavities of basalt at Spokane; they have the form of cubo-octahedra. L. J. S.

**Becquerelite, a New Radioactive Mineral.** Alfred Schoep (*Compt. rend.*, 1922, **174**, 1240—1242).—This mineral occurs as canary- to orange-yellow, crystalline crusts on pitchblende from the Kasolo mine, Katanga, Belgian Congo. Minute crystals are orthorhombic with perfect (001) and (110) cleavages. The acute negative bisectrix emerges through (001). The mean of two analyses on material dried at 100° gave :

| $UO_3$. | $Fe_2O_3$. | PbO. | $SiO_2$. | $SO_3$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|
| 86·51 | 0·54 | 5·25 | 0·83 | 1·01 | 5·82 | 99·96 |

Needles of anglesite and crystals of curite (this vol., ii, 77) and soddite (this vol., ii, 451) are present; and microchemical tests of the canary-yellow material show only traces of lead. Deducting lead, etc., and adding water (4·21%) lost at 100°, the formula is deduced as $UO_3,2H_2O$. L. J. S.

**Sincosite, a New Mineral.** Waldemar T. Schaller (*J. Washington Acad. Sci.*, 1922, **12**, 195).—This forms green, rectangular plates, which are optically uniaxial (sometimes biaxial) and negative, in black carbonaceous shale near Sincos, Peru. Analysis :

| CaO. | $V_2O_4$ | $P_2O_5$. | $H_2O$. | Insol. | Total. |
|---|---|---|---|---|---|
| 12·1 | 36·3 | 31·7 | 19·9 | 0·3 | 100·3 |

gives the formula $CaO,V_2O_4,P_2O_5,5H_2O$. Since the mineral belongs to the uranite group (autunite, torbernite, etc.), the "equivalent valency" of quadrivalent vanadyl-vanadium with sexavalent uranic-uranium is suggested. L. J. S.

**Optical-crystallographic Properties of Calcium Oxalate Monohydrate.** Edgar T. Wherry (*J. Washington Acad. Sci.*, 1922, **12**, 196—200).—The crystallographic and optical constants

hitherto determined for the mineral whewellite are tabulated, and the relation of the optical orientation to the various habits of the crystals is pointed out. Fragments of the mineral, crystals from plant tissues, and crystalline precipitates (prepared by boiling together solutions of the constituent ions) were examined microscopically. Refractive indices, $\alpha$ 1·490, $\beta$ 1·555, $\gamma$ 1·650.

L. J. S.

**The Chemical Constitution of Felspars. Analysis of Two Microclines.** M. E. DENAEYER (*Bull. Soc. chim. Belg.*, 1922, **31**, 131—147).—Theories of the constitution of complex silicates (W. and D. Asch, "Die Silicate," Berlin, 1911; P. Erculisse, "*Classification chimique des silicates naturels*," Brussels, 1920; J. Jakob, A., 1920, ii, 754) are discussed, and an attempt is made to apply Werner's co-ordination theory to the problem. Some formulæ based on the latter theory are given and a pseudo-phase rule diagram based on these is used to suggest the mutual relationship of quartz, orthose, plagioclases, micas, and spinels. The connexion between the views put forward by Jakob and by F. W. Clarke is briefly discussed.

The analysis of two microclines (triclinic potash-soda felspars) is considered to indicate that they are built up of three separate components in solid solution, and a study of results of analyses carried out by other workers tends to confirm this view.

H. J. E.

**Soddite, a New Radioactive Mineral.** ALFRED SCHOEP (*Compt. rend.*, 1922, **174**, 1066—1067).—This forms with curite (A., 1922, ii, 77) fine-grained crystalline aggregates at Kasolo, Katanga, Belgian Congo. In veins in this material minute prismatic crystals were found which from their optical characters are orthorhombic. *H* 3—4, $d^{17}$ 4·627. Heated in a bulb-tube the mineral gives off water and oxygen and turns black, and it is infusible before the blow-pipe. The mean of several partial analyses is:

| $SiO_2$. | $UO_3$. | $Fe_2O_3$. | $H_2O$. |
|---|---|---|---|
| 7·83 | 85·33 | 0·40 | 6·23 |

agreeing with the formula $12UO_3,5SiO_2,14H_2O$. L. J. S.

**Ore Deposits and their Genesis in Relation to Geographical Distribution.** A Lecture Delivered before the Chemical Society on December 8th, 1921. JOHN WALTER GREGORY (T., 1922, **121**, 750—772).

**Meteoric Iron from Odessa, Ector Co., Texas.** GEORGE P. MERRILL (*Amer. J. Sci.*, 1922, [v], **3**, 335—337).—The much rusted fragment of 1120 grams as received was stated to be from a larger mass found near Odessa. The etched surface shows a coarse octahedral structure. Analysis by E. V. SHANNON gave:

| Fe. | Ni. | Co. | Cu. | Pt. | Cr. | Mn. | C. | P. | S. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 90·69 | 7·25 | 0·74 | 0·02 | nil | trace | nil | 0·35 | 0·23 | 0·03 | 99·31 |

L. J. S.

**Meteoric Irons from Alpine, Texas, and Signal Mountain Lower California.** George P. Merrill (*Proc. U.S. Nat. Mus* 1922, **61**, art. 4, 1—4).—A fragment of a mass, said to weigh tw tons, from Alpine shows the finely granular structure of an ataxite and gave anal. I by J. E. Whitfield. A fragment from a mass said to have been observed to fall at Signal Mountain severa years ago, gave II. The medium octahedrite structure grade into a finely granular structure at the exterior of the mass, th latter structure having evidently resulted by the heating durin flight through the earth's atmosphere.

| | Fe. | Ni. | Co. | Cu. | S. | P. | C. | Si. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I | 93·60 | 5·62 | 0·43 | 0·016 | 0·012 | 0·328 | 0·008 | 0·015 | 100·02 |
| II | 91·47 | 7·86 | 0·60 | 0·015 | 0·002 | 0·041 | — | 0·004 | 99·99 |

A pallasite from Cold Bay, Alaska, is also briefly described.

L. J. S.

## Analytical Chemistry.

**The Application of Conductometric Methods to Precipitation Analysis.** I. M. Kolthoff (*Z. anal. Chem.*, 1922, **61**, 171—180).—The author discusses the conditions necessary for obtaining good results by conductometric methods in precipitation analysis and details the possible sources of error under three headings: errors in the determination of the conductivity, errors due to the solubility of the precipitate being too great, and errors due to the composition of the precipitate not being constant. In the first case, the analysis is more exact the slower the rate of migration of the ions taking the place of those precipitated, whilst the end-point is sharper the greater the speed of the anion which is precipitated and the greater the degree of dissociation of the salt. The speed of the ions present which take no part in the reaction is immaterial, but, as the presence of indifferent electrolytes decreases the accuracy of the method, they should be kept as low as possible and the reagent used for precipitation must be a strong electrolyte. The solubility of the precipitate must, at the most, not exceed a normality corresponding with one-twentieth of the normality of the solution from which it is produced. Errors may arise owing to the slow rate at which the precipitate forms or to adsorption of salts by the precipitate; the former may be overcome by the addition of alcohol to the solution. A. R. P.

**Estimation of Hydrogen-ion Concentration in Urine with Indicators.** Adolf Silberstein (*Biochem. Z.*, 1922, **128**, 534—539).—The colorimetric estimation of the $P_H$ of coloured liquids like urine is simplified by removing the natural colouring matter by shaking with charcoal, for instance, "Carbo medic," Merck. There is no change of $P_H$ after this treatment of urine. H. K.

**Reaction between Thiosulphuric and Nitrous Ions.** P. FALCIOLA (*Gazzetta*, 1922, **52**, i, 179—182).—If sodium thiosulphate, even in very dilute solution, is treated with dilute sodium or potassium nitrite solution and the liquid is then acidified with either an inorganic or organic acid or a salt, such as alum, giving an acid solution, more or less marked effervescence occurs and the solution assumes a yellow colour which, according to the amounts of the substances used, may at first be green or orange-brown. The reaction is equally sensitive in aqueous alcoholic solution and is shown distinctly by 0·0001*N*-sodium thiosulphate solution, which does not readily yield sulphur when treated with a mineral acid or give a coloration with ferric chloride. Only excessive proportions and concentrations of sulphurous acid prevent the reaction with traces of thiosulphate. The nitrous ion in presence of the nitric ion may be detected by means of the reaction (cf. Bodnár, A., 1914, ii, 67). T. H. P.

**The Volumetric Estimation of Dithionates.** A. FISCHER and W. CLASSEN (*Z. angew. Chem.*, 1922, **35**, 198—199).—Sodium dithionate is not attacked by cold alkaline or neutral oxidising agents and but little in acid solution. On heating with acid, evolution of sulphur dioxide commences and oxidation follows. Attempts to devise a direct titration with an acid oxidising agent were unsuccessful either through loss of sulphur dioxide or through secondary reactions. A method was therefore adopted of distilling the sulphur dioxide into a known volume of an oxidising agent. Potassium permanganate and dichromate proving unsuitable, iodine solution was employed. The sodium dithionate is weighed into a flask, distilled hydrochloric acid free from chlorine added, and a stream of carbon dioxide passed through the apparatus. The flask is then heated and at the end of the reaction carbon dioxide is again passed through the apparatus. The results are in close agreement with those of gravimetric analysis. The method may be applied to mixtures of dithionates with other sulphur salts, most of which are decomposed by cold hydrochloric acid or oxidised by alkaline hydrogen peroxide. C. I.

**Estimation of Ammonia in Urine by Schlœsing's Bell-glass Method.** W. MESTREZAT and (MLLE) M.-P. JANET (*Bull. Soc. Chim. Biol.*, 1922, **4**, 154—164).—Schlœsing's method is modified and used for the estimation of ammonia in urine. To 20 c.c. of urine contained in a desiccator are added a few drops of sulphuric acid to dissolve any ammonium magnesium phosphate, and five drops of a 10% solution of mercuric cyanide to prevent bacterial decomposition of urea. Ten c.c. of 20% milk of lime are then added, after which a basin containing 10 c.c. of 0·1*N*-sulphuric acid is rapidly placed on a tripod in the desiccator and the latter closed. After remaining for three days at a room temperature of 15—20°, the excess of acid is titrated. No appreciable quantity of ammonia is evolved from nitrogenous organic substances present in the urine. E. S.

**The Estimation of Ammoniacal Nitrogen in Nitrogenous Organic Substances, and particularly in Proteins and their Products of Decomposition.** J. Froidevaux (*Compt. rend.*, 1922, **174**, 1238—1240).—To 15 c.c. of the solution under examination 35 c.c. of 60% aqueous sodium hydroxide are added and air, carefully freed from ammonia, is bubbled through at the ordinary temperature at the rate of 150—200 bubbles per minute. The issuing air is passed through a known volume of standard acid. The acid is replaced from time to time and titrated. The ammonia absorbed is plotted against the time. The resulting curve consists of a line sharply inclined to the time axis and a line slightly inclined to the same axis, these being joined by a curved portion. The first line corresponds with ammoniacal nitrogen and the second line with ammoniacal nitrogen coming from the slow decomposition of protein or amino-acids. The curved portion is a combination of the two. The two lines are produced to meet and their junction represents the total ammoniacal nitrogen originally present as such in the sample. W. G.

**The Analysis of Liquid Nitrogen Peroxide.** A. Sanfourche (*Bull. Soc. chim.*, 1922, [iv], **31**, 316—319).—The sampling is done by means of a Durand washing flask, the central tube of which is drawn out to a fine orifice, the flask being kept immersed in ice.

For the estimation of nitric acid in the sample, 10 c.c. of the liquid are measured out into a cylindrical gas-drying tube, which is then surrounded with ice, and air is bubbled through the liquid until the whole of the nitrogen peroxide has evaporated. The residual nitric acid, which should not evolve nitrous vapours when warmed by the hand, is diluted with water and titrated with *N*-sodium hydroxide.

For the estimation of nitrogen peroxide and nitrous anhydride, a known volume of the sample is dissolved in 20 c.c. of concentrated sulphuric acid cooled in ice, and aliquot portions of the solution are titrated with *N*/10-permanganate, and analysed in a Lunge nitrometer, respectively. From these results it is possible to calculate the percentages of nitrogen peroxide and nitrous anhydride respectively in the sample. W. G.

**Estimation of Nitrates in Drinking Water by Mayrhofer's Method.** A. Reuss (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 174—183).—The consumption of indigotin solution is considerably increased in the presence of sodium chloride, the reaction between small quantities of nitrates and the indigotin being facilitated by this substance. If only small quantities of nitrates and small quantities of chlorides are present in the water, it is advisable to add sufficient sodium chloride to bring the concentration up to 1 gram per litre. The indigotin solution must then be standardised against a nitrate solution containing 1 gram of sodium chloride per litre. Mayrhofer's tables can then be used. The indigotin solution must not have the slightest sediment or its titre will be variable. It is best filtered through asbestos without suction until no suspended particles are visible with a lens. The solution should

be added at a rate of 2—3 drops per second, the last drops being added at a somewhat slower rate. Care must be taken that the whole of the 5 c.c. of sulphuric acid actually reach the liquid in the flask. The acid used must be of the same composition as that used in standardising the indigotin solution which should be prepared as described by Lehmann in an appendix to the paper.

H. C. R.

**The Estimation of Inorganic Phosphorus in Blood Plasma by Bell and Doisy's Method.** BURTON A. MYERS and MARIAN C. SHEVKY (*J. Lab. Clin. Med.*, 1921, 7, 176—180; cf. A., 1920, ii, 769).—Phosphorus was not recovered quantitatively from plasma by Bell and Doisy's method, when added in known quantity. The only solution correctly measured was one which was weaker than the standard; all stronger than the standard showed considerable minus errors. This difficulty was obviated by using a series of standards of such strength that one might be chosen containing approximately 0·25 mg. per 100 c.c. more phosphorus than the unknown. A small series of estimations thus made gave an error ranging from 2·3 to 10% with an average of 5·8%. In many rabbit plasmas and some human plasmas larger amounts of molybdic acid and quinol solutions than prescribed in the original directions must be used to develop the proper colour. 1·5 c.c. of molybdic acid and 3 c.c. of quinol for each 5 c.c. of plasma filtrate (1 : 5 dilution) are recommended.

CHEMICAL ABSTRACTS.

**Qualitative Reactions for Arsenic.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 334—350).—The reactions of Mayençon and Bergeret (this Journal, 1874, 1008; reduction to arsine and detection with mercuric chloride paper), Bougault (reduction to free arsenic by use of hypophosphite), Bettendorf (reduction to arsenic, using stannous chloride), and Reinsch have been examined. The most suitable is the first, which under the conditions recommended will detect one-millionth of a gram (1 $\mu$.g.) in 1 c.c. To 1 c.c. of the neutral solution are added 1 c.c. of 22% hydrochloric acid containing 1% of stannous chloride, and 0·1 gram of finely divided aluminium foil. The gas is led through cotton-wool on to a strip of paper 4 mm. wide prepared by saturating filter-paper in 5% aqueous mercuric chloride solution. After one hour the colour of the paper is examined. Antimony must be removed by treating the paper with hydrochloric acid or potassium iodide.

Mercury salts interfere strongly, copper salts moderately; salts of other metals do not seriously affect the test.

Bougault's reaction will detect 2 mg. of arsenic per litre. Two c.c. of the solution, admixed with 1 c.c. of the reagent, and 4 c.c. of strong hydrochloric acid, are heated in the water-bath for thirty minutes. A brown colour shows presence of arsenic. The solution may be filtered, a stain remaining on the paper. S. I. L.

**Aluminium for the Arsenic Reaction.** G. ROMIJN (*Chem. Weekblad*, 1922, **19**, 177—179).—The author agrees with Kolthoff

(preceding abstract) that aluminium is to be preferred to zinc which he had formerly recommended (Romijn, *Pharm. Weekblad* 1917, **54**, 1216), in the Mayençon and Bergeret reaction. He detail some improvements in the apparatus which allow of the detectior of 0·5 μ.g. of arsenic with a reaction time of two to five minutes He suggests that in presence of formaldehyde hexamethylene tetrarsine may be formed. S. I. L.

**Estimation of Volatile Matter in a Coal.** A. DESSEMONI (*Rev. ind. min.*, 1921, **1**, 451—456).—The essential analytica operations for estimating the volatile substances and ash of a coa by desiccation, distillation, and incineration are discussed. In the formula $V=v/(100-c)$, where $c=\%$ ash, $v=\%$ volatile substances in the crude coal, and $V=\%$ volatile substances exclusive of the ash, calculations show that the percentage of $V$ increases as the percentage of ash increases and becomes infinite when the ash becomes 100. A general investigation of the formula and of the errors usual in the procedures has led to the proposal of a simple formula expressing the content of volatile substances in a coal exclusive of the ash: $V=[v-(c/n)]/(100-c)$, where $n$ is a variable coefficient depending on the impurities. Numerous samples of coal are given, and it is suggested that the value $n=10$ be adopted as a sufficiently accurate approximation for most coals. CHEMICAL ABSTRACTS.

**The Separation of Zinc by Means of Ammonium Phosphate.** G. LUFF (*Chem. Zeit.*, 1922, **46**, 365—366).—Magnesium and manganese may be separated quantitatively from zinc by precipitation with ammonium phosphate in solutions containing at least one-fifth of their bulk of ammonia (*d* 0·923), whilst iron and aluminium may be precipitated as phosphates free from zinc by addition of ammonium phosphate to the solution containing at least one-fifth of its bulk of glacial acetic acid. The zinc is recovered from the filtrate by rendering it neutral to litmus, in the first case with hydrochloric acid, and in the second case with ammonia. The separation of manganese and zinc must be carried out in an atmosphere of hydrogen to prevent precipitation of manganese dioxide. [Cf. *J. Soc. Chem. Ind.*, 1922, June.] A. R. P.

**An Electro-volumetric Method for Lead.** D. A. MACINNES and ERIC B. TOWNSEND (*J. Ind. Eng. Chem.*, 1922, **14**, 420—421).—The solution containing the lead as nitrate together with free nitric acid is electrolysed with a current of 13 amperes for thirty to forty-five minutes in a platinum dish, 9 cm. in diameter and roughened on the inside, which acts as anode whilst the cathode consists of a small platinum disk rotated at 600 revolutions per minute. The deposit is washed with cold water and dissolved in an excess of standard oxalic acid and 5 c.c. of nitric acid heated at 80°. The solution is rinsed into a beaker, a few c.c. of sulphuric acid are added, and the excess of oxalic acid is estimated by titration with permanganate. The results prove that the deposit consists entirely of lead dioxide with variable amounts of water, and that, contrary to previous statements, it contains no higher oxides.

The method described is more exact than that of weighing the deposit and calculating the lead by using an empirical factor, as the amount of water in the deposit varies with its weight.

A. R. P.

**Red Coloration of Sodium Hypochlorite Solutions.** TEALDI MARIO (*Boll. Chim. Farm.*, 1922, **61**, 165—166).—Sodium hypochlorite prepared from chemically pure calcium hypochlorite and sodium hydrogen carbonate develops no red coloration, and the presence of manganese in the glass of the containing vessel neither induces the coloration nor enhances the intensity of solutions already reddened. If commercial reagents are used in its preparation the salt at once turns red, irrespective of the presence of manganese in the reaction vessel. The coloration is not modified by addition of an iron salt, but is destroyed by sodium thiosulphate. The conclusion is drawn that the red colour is due to salts of permanganic acid derived from the manganese in the reagents used.

T. H. P.

**Chemical Analysis with Membrane Filters. III. Their Application to Volumetric Analysis.** GERHART JANDER (*Z. anal. Chem.*, 1922, **61**, 145—171).—Membrane filters are particularly suited to volumetric work involving precipitation of a definite compound followed by solution of the precipitate and titration, owing to the ease with which the precipitate can be removed from the filter simply by spraying water over it. The estimation of calcium by precipitation and titration of the oxalate with permanganate, of manganese by precipitation of the sulphide followed by solution of the latter in standard acid and titration of the excess acid with alkali, and of chromic acid in the presence of other oxidising acids is described in detail.

The estimation of manganese is carried out by treating the solution, 70 c.c., containing not more than about 0·25 gram of metal with 30 c.c. of 10% ammonium chloride solution, a few c.c. of ammonia and, after boiling, a large excess of freshly prepared ammonium sulphide solution. Boiling is continued for ten minutes to change the precipitate into the green modification, more ammonium sulphide is added, and the solution is cooled and filtered on a " 30—60 second " membrane filter. The precipitate is washed first with water containing ammonium sulphide, then with neutral 2% sodium sulphate solution, rinsed off the filter with cold water, and dissolved in 60 c.c. of $N/5$-sulphuric acid. The solution is boiled to expel hydrogen sulphide, cooled, and titrated with $N/5$-sodium carbonate solution, using methyl-orange as indicator.

The volumetric estimation of chromium as chromate in solutions containing other oxidising substances, for example, chlorates or bromates derived from the oxidation of tervalent chromium to the sexavalent form in alkaline solution by means of chlorine or bromine, is carried out as follows: the solution is just acidified with acetic acid, 20 c.c. of $N$-sodium acetate solution are added, and the chromic acid is precipitated from the boiling solution by the addition, drop by drop, of a slight excess of $N/10$-lead acetate

solution. After cooling, the precipitate is collected on a membran filter, washed with cold water, rinsed back into the beaker, an dissolved in 100 c.c. of *N*-hydrochloric acid. An excess of standard solution of ferrous sulphate is added and the excess i estimated by titration with potassium dichromate as usual.

A. R. P.

**The Estimation of Cobalt in Steel.** ALOIS EDER (*Chem. Ztg.* 1922, **46**, 430).—The method depends on the separation of th iron from a weakly acid sulphate solution by means of an emulsio of zinc oxide and precipitation of the cobalt in an aliquot part o the filtrate after acidification with hydrochloric acid by means o an excess of a solution of nitroso-β-naphthol in 50% acetic acid followed by ignition of the precipitate mixed with oxalic acid t the oxide $Co_3O_4$, which is weighed. [Cf. *J. Soc. Chem. Ind.*, 1922 June.]

A. R. P.

**Detection and Estimation of Small Quantities of Nicke and Cobalt in Silicate Rocks.** O. HACKL (*Chem. Ztg.*, 1922 **46**, 385—386).—A large quantity of the sample is digested wit aqua regia, the filtered solution is evaporated to expel nitric acid the residue digested with hydrochloric acid, the solution dilute with water, treated with hydrogen sulphide, filtered, and th filtrate made ammoniacal and saturated again with hydroge sulphide. A large excess of 5% hydrochloric acid is added, th solution set aside until the precipitate has settled, and then filtered the precipitate being washed with dilute hydrochloric acid solutio saturated with hydrogen sulphide. It is dissolved in aqua regi and the solution divided into two parts, one of which is tested fo nickel by means of α-dimethylglyoxime in weakly ammoniaca tartaric acid solution, and the other for cobalt, after removin the trace of iron present by any suitable method, by Vogel's thio cyanate reaction or by means of nitroso-β-naphthol. The quanti tative estimation of the metals is made in the same way, excep that the sulphide precipitate after dissolving in aqua regia is free from iron by triple precipitation of the solution with ammoni or by precipitation with barium carbonate. Nickel and cobal are again precipitated as sulphides in the filtrate from the iron the sulphides are ignited to oxides, and these reduced to and weighe as metals. Either the nickel or the cobalt is then estimated an the other found by difference. In all cases, the insoluble residu from the original aqua regia treatment of the ore must be teste for the presence of nickel and cobalt by dissolving it in hydro fluoric acid and testing the solution as described above.

A. R. P.

**A Modified Reaction of Tin.** HANS HELLER (*Z. anal. Chem.* 1922, **61**, 180—182).—The following modification of the iodid method for the detection of tin gives more trustworthy result than that recommended by Mazuir (A., 1920, ii, 197). One c.c of the solution containing only a little hydrochloric acid is mixe with 0·5 c.c. of 5% potassium iodide solution and 0·5 c.c. of stron

sulphuric acid is introduced, by means of a pipette, below the surface of the liquid. If tin is present an immediate precipitate of yellow iodide forms at the surface between the two liquids. The precipitate dissolves readily on addition of hydrochloric acid and careful shaking. Arsenic and antimony interfere with the test.

A. R. P.

**The Volumetric Estimation of Titanium Dioxide in Bauxite.** H. J. WINCH and V. L. CHANDRATREYA (*Chem. News*, 1922, **124**, 231—232).—0·3 Gram of the sample is dissolved by fusion with 3 grams of potassium pyrosulphate and the fused mass is dissolved in hydrochloric acid. The solution is boiled with 0·15 gram of tin powder and 5 grams of ammonium chloride until all the tin has dissolved. Cold water is added to the liquid followed by 50 c.c. of 4% mercuric chloride solution to destroy excess of stannous chloride (titanous chloride is not oxidised by mercuric chloride in the cold) and 5 c.c. of ferric chloride solution containing 10 grams of iron per litre. The liquid is then titrated with potassium dichromate as usual. The iron is determined in a separate sample by reduction with stannous chloride followed by titration with the same dichromate solution. The difference in the two readings corresponds with the titanium dioxide present. A. R. P.

**Detection and Estimation of Vanadium in Steels.** GEORGES MISSON (*Bull. Soc. chim. Belg.*, 1922, **31**, 123—126).—A colorimetric method of estimating vanadium is described, for which considerable accuracy is claimed. The steel is dissolved in nitric acid, any organic matter oxidised by means of permanganate, and, after oxidising any precipitated oxide of manganese with a solution of sodium peroxide in dilute nitric acid, a further quantity of the latter reagent is added in order to produce the colour for comparison. It is essential that all the reagents should be free from chlorine. Modifications are described which render the method applicable to steels containing tungsten, chromium, and nickel. H. J. E.

**Detection of Traces of Osmium by Means of Potassium Thiocyanate.** MAX HIRSCH (*Chem. Ztg.*, 1922, **46**, 390).—The metal to be tested for osmium is dissolved in fuming nitric acid or by fusion with sodium hydroxide and potassium nitrate or chlorate, followed by solution of the fused mass in water and acidification of the solution with nitric acid. In either case, the solution is distilled and the distillate collected in cold water. This solution is acidified, concentrated potassium thiocyanate solution added, and the whole shaken with ether or amyl alcohol. A blue colour in the ethereal layer indicates osmium. The colour is just perceptible at a dilution of 1 part of osmium per million parts of solution. A. R. P.

**The Clarification of Solutions containing Reducing Sugars by Basic Lead Acetate. The Effect of Different Deleading Agents.** DUANE T. ENGLIS and CHUK YEE TSANG (*J. Amer. Chem. Soc.*, 1922, **44**, 865—867).—The removal of excess of basic

lead acetate, used as a clarifying agent from solutions of dextros or lævulose results in the loss of sugar. Of the agents triec namely, potassium oxalate, disodium hydrogen phosphate, potassiur sulphate, potassium sodium tartrate, and sodium carbonate, th least loss of sugar occurred when disodium phosphate was used. I general, the loss of lævulose is much greater than that of dextrose. ] the precipitate is washed, a much smaller loss is observed. W. G.

**Detection of Lactic Acid in Organic Liquids.** F. D'Arbel (*Rend. accad. med.-fis. fiorentina ; Sperim.*, 1921, **75**, 415—416).—Pittarelli's method (A., 1921, ii, 418) is not specific, as the coloratio is given by many other substances. Uffelmann's reaction i preferred. CHEMICAL ABSTRACTS.

**The Analysis of Solutions of Ammonium Citrate.** C. S Robinson and Selma L. Bandemar (*J. Ind. Eng. Chem.*, 192: **14**, 429—432).—The methods proposed for the determination c the ratio of ammonia to citric acid in ammonium citrate solution have been examined and the results obtained are tabulated. Th formaldehyde method invariably yields accurate results provide sufficient of the reagent is added to combine with all the ammoni and the addition of alkali is carried to the first permanent pin colour of the phenolphthalein. The only other method that give accurate results is as follows: 50 c.c. of the solution are dilute to 500 c.c. and 10 c.c. trials are distilled with an excess of standar alkali to obtain the ammonia. The residue in the distillatio flask is titrated with standard acid until the solution is distinctl acid to methyl-red; it is then boiled to expel carbon dioxide, few drops of phenolphthalein are added, and the solution is titrate with standard alkali hydroxide until a permanent pink colour i obtained. The difference between the total alkali and acid used give the amount of alkali used in neutralising the citric acid. A. R. P.

**Golodetz's Reaction (The Benzoyl Peroxide Reaction)** H. C. J. H. Gelissen (*Rec. trav. chim.*, 1922, **41**, 224—227).—Golodetz's reaction (A., 1908, ii, 330) is not specific for benzoy peroxide, but is given by all peroxides which, on treatment wit concentrated sulphuric acid, yield phenolsulphonic acid. It ma therefore be regarded as based on Hehner's reaction. Liebermann test and Millon's test for phenol apply equally to benzoyl peroxid under the conditions indicated for Golodetz's reaction. A modif cation of Golodetz's procedure is recommended, as the test is con siderably more sensitive if the sulphuric acid is cooled to —2C instead of being gently heated; the tests for phenol are also cleare at the lower temperature. H. J. E.

**Indican Reactions for the Detection of Urine in Stain** Giuseppe Jemma (*Arch. Farm. sperim. Sci. aff.*, 1921, **32**, 193-194).—Replacement of thymol by α-naphthol in the applicatic of Jolles's test (A., 1915, ii, 593, 655) to the detection of urine stains (Latta, A., 1920, ii, 339) renders the reaction from two t four times more sensitive. The use of α-naphthol-*p*-sulphonic ac with this test leads, however, to unsatisfactory results. T. H. P.

## General and Physical Chemistry.

**Spectrum of Hydrogen.** T. R. Merton and S. Barratt (Bakerian Lecture, *Phil. Trans.*, 1922, [*A*], **222**, 369—400).—The wave-lengths of about 1200 lines in the secondary spectrum have been measured and classified into physically related groups according to the effects of the pressure of the gas, electrical excitation, and the presence of helium. This method of classification has been compared with the results of other investigators relating to the Stark and Zeeman effects and with the regularities observed by Fulcher. By means of a new method of measuring the widths of spectrum lines, it is shown that the secondary spectrum is due to hydrogen molecules. No evidence of the presence of secondary hydrogen has been found in the spectra of the sun. The effect of impurities and changes in the methods of electrical excitation on the relative intensities of the Balmer and secondary series is discussed, and it is shown that the greater the purity of the hydrogen the more prominent the secondary spectrum. The light from different portions of the capillary of the discharge tube varies in character with the nature of the discharge. With a condenser and spark gap in the electrical circuit, a mixture containing hydrogen aud helium gives the hydrogen line at the two ends of the tube. Mercury lines and the lines of the heavier elements appear in the middle of the tube. On cutting out the condenser, this unequal distribution slowly changes. A partial separation of the gases in the discharge tube would explain these phenomena and the observation of Wood (cf. A., 1921, ii, 665) with long vacuum tubes, that the Balmer series are strongest in the middle of the tubes.

W. E. G.

**Excitation of Gas-spectra during Chemical Reactions.** F. Haber and W. Zisch (*Z. Physik*, 1922, **9**, 302—326).—A continuation of the work of Haber and Just (cf. A., 1911, ii, 954) on the emission of electrons in chemical reactions. The nature of the light emitted from flames of sodium and mercury burning in the halogens is investigated. Sodium vapour, diluted by nitrogen, is burnt in chlorine, bromine, iodine, or oxygen, the concentrations being so adjusted that the temperature of the flame is maintained below the limit at which temperature radiation becomes visible. With chlorine, a luminosity, greyish-green in appearance, is first observed at 350—360°. At higher temperatures, it becomes yellow, and at 473° is of sufficient intensity to make it possible to photograph the sodium doublet. The source of the *D*-line is the free sodium atom which is activated by collision with a freshly formed molecule, NaCl or $NaCl_2$, which has not yet dissipated its energy of combination. It is considered that the conductivity and luminosity of the inner cone of the Bunsen flame are partly chemical in origin and this view is supported by the intense colour of the inner cone when an alkali metal is added to the flame.

Mercury, burnt under similar conditions, gives a green cone wi a band showing maxima between 595 $\mu\mu$ and 300 $\mu\mu$, whereas tl wave-length, corresponding with the heat of formation of mercur chloride, is 546 $\mu\mu$.

The conductivity of oxygen and potassium vapour at low pressur is considerable, so that electrically charged particles, possib electrons, are liberated. New determinations of the vapour pressu of sodium vapour between 473° and 563° have been made. Tl relationship between light and electron emission during chemic reaction is discussed. In light emission, the excitation of tl electron takes place from the normal state to the first quantu orbit, whereas in electron emission the electron is raised to a infinitely large orbit. W. E. G.

**Doublets in the Visible Spectrum.** S. GOUDSMIT (*Arc. Néerland,* 1922, [iii], **6**, 116—126).—Diverse empirical relationshi have been found between the doublets in the visible spectrun Sommerfeld gives $\Delta\nu=0{\cdot}365\ (Z-z)^4$; where $\Delta\nu$ is the breadt of the doublet in cm.$^{-1}$, $Z$ is the nuclear charge or atomic numbe and $z$ is the number which indicates the "screening effect" the electrons; Sommerfeld calls $(Z-z)$ the effective nuclear char $(Z_{eff})$. From this equation he has deduced the effective nucle charge from the $L$-doublets, the difference between this and tl true nuclear charge gives the screening effect of the $L$-series, an the mean value 3·63 was obtained. It is here assumed that $Z$ has the same value at all points on the orbit of the electron, bu whilst this may be true in the case of a circular orbit, it cann hold when the orbit is an ellipse. Lithium gives a spectrum closel resembling that of hydrogen, the doublet $2\,p$ being almost of th same magnitude. The present author investigated whether th doublet and as a result all the doublets in the spectra hav not the same origin as that of hydrogen, that is, that they we due to relativity. This point of view is contradictory to the wel established theory of Sommerfeld concerning the origin of th spectral series, but the results obtained were in good agreemen The objections to this method of treatment are discussed.

W. T.

**The $L$-Series of the Elements Barium to Rubidium.** I COSTER (*Arch. Néerland,* 1922, [iii], **6**, 76—91).—The author give the wave-lengths and intensities of the $L$-series of these element found by Hjalmar (A., 1921, ii, 145) and himself, using the metho of Siegbahn. The values found differ somewhat from those foun by Siegbahn. The results are discussed in detail on the basis o Bohr's new theory (this vol., ii, 277). W. T.

**Observations on the Rare Earths. XI. The Arc Spectrum of Yttrium.** L. F. YNTEMA and B. S. HOPKINS (*J. Opt. Soc Amer.,* 1922, **6**, 121—134).—A determination of the emissio spectrum of yttrium. The yttrium material which containe of 0·005% of holmium was obtained in the work on atomic weight with the University of Illinois. The spectrum, however, showe

that other rare earth elements, erbium and dysprosium, and also magnesium and silicon, were present in small amounts. The yttrium material has a few lines in common with the eurosamarium of Eder. A comparison is made with the values previously obtained by Eder.

W. E. G.

**The *L*-Series of Lutecium and Ytterbium and the Identification of Celtium with the Element of Atomic Number 72.** A. DAUVILLIER (*Compt. rend.*, 1922, **174**, 1347—1349).—By a modification of his previous technique (cf. A., 1921, ii, 421, 475, 669), the author has been able to make a detailed study of the *L*-series of lutecium and ytterbium in the form of their oxides. Twenty-six rays have been identified for lutecium, and the wave-lengths of these together with those for ytterbium are tabulated. In addition, the existence of some feeble lines indicated the presence of a trace of thulium. These lines were $\gamma_7=1272{\cdot}1$; $\gamma_1=1311{\cdot}3$; and $\beta_2=1456{\cdot}3$. Further the existence of two very feeble lines, $\beta_2=1319{\cdot}4$ and $\alpha_1=1561{\cdot}8$, show the existence of a trace of celtium and assign to it the atomic number 72. This element had been discovered in the same preparation by Urbain (A., 1911, ii, 115) by the appearance of a group of unknown lines in the arc spectrum.

W. G.

**The *N*-Series of Röntgen Spectra.** V. DOLEJŠEK (*Z. Physik*, 1922, **10**, 129—136).—With the aid of the spectrograph of Siegbahn (*Z. Physik*, 1922, **9**, 68), determinations have been made of the *N*-series of uranium, thorium, and bismuth. All these lines were severely tested, to eliminate the *M* lines of higher order, by absorption through different thicknesses of aluminium and black paper and by a comparison of the spectra reflected from different crystals. A scheme of the *N* lines of the gas niton (86) shows the presence of seven *N*, five *O*, and three *P* levels in the atom. The various modes of transference of the electrons between these levels are also indicated. All the lines which have been found ($\lambda$ 8,594—$\lambda$ 13,255) agree with the theoretical expectations, and all possible lines, except that due to the transference between $N_7$ and $O_4$, have been observed. The $P_1$—$P_2$ and $O_1$—$O_2$ doublets have been separated for the first time. The hardest lines of the *N*-spectra for the three metals follow the Moseley frequency relation.

W. E. G.

***X*-Ray Spectra.** WILLIAM DUANE and R. A. PATTERSON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 85—90).—In view of certain criticisms of their previous work, the measurements of the *L*-absorption limits of platinum, gold, and bismuth (cf. A., 1920, ii, 407) have been repeated with increased accuracy. The absorption limits are found to possess somewhat shorter wave-lengths than the shortest emission lines associated with them. The authors have also measured the absorption spectrum for the *K*-series of molybdenum, and there are considerable discrepancies between their measurements and those of Overn (*Physical Rev.*, 1921, **17**, 350). The ratio of the intensities of $\alpha_1$ to $\alpha_2$ is given as 1·97 as

compared with 2·00 predicted by Bohr. The ratio of the intensities of $\beta$ to $\gamma$ in the first order is 6·3, and in the second order is 5·46.

W. E. G.

**A Chromophore Grouping of Atoms in Inorganic Triple Salts and a General Theory for the Cause of the Colours of Substances.** HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], **3**, 417—422).—The author finds that complex salts containing the same metal in different states of valency are highly coloured, and he suggests that there is a constant exchange of electrons between the atoms of different valency and that this activity of electrons affects the passage of light, producing colours or opacity. An attempt is also made to extend this theory to explain the colours of substances in general by assuming spontaneous exchanges of electrons which affect the passage of light. W. T.

**The Labile Nature of the Halogen Atom in Organic Compounds. III. The Absorption Spectra of Bromomalonic Derivatives and Nitroparaffins, and their Bearing on the Question of an Oxygen-Halogen Linking.** HUGH GRAHAM and ALEXANDER KILLEN MACBETH (T., 1922, **121**, 1109—1115).

**The Relationship between Chemi- and Photo-luminescence in Unsaturated Silicon Compounds.** H. KAUTSKY and H. ZOCHER (*Z. Physik*, 1922, **9**, 267—284).—The compounds obtained by the action of acids on calcium silicide, for example, oxydisilin, silical hydroxide, and leucone (cf. A., 1921, ii, 505) have been further investigated. Chemiluminescence occurs when silicones, mixtures of oxydisilin, and silical hydroxide, are oxidised by chromic acid or potassium permanganate in acid solution. The colour of the silicones varies from pale yellow to deep red as the concentration of silical hydroxide increases, and the chemiluminescence follows identical colour changes. Oxidisilin gives only a feeble green light, and the dark red silical hydroxide a dark red light. Similar changes in colour occur for mixtures of silical hydroxide and leucone, and the latter, a white substance, shows no chemiluminescence. The photochemical oxidation of oxydisilin with ethyl iodide and water by short wave-lengths of light is accompanied by the emission of light of long wave-length. The intensity of the photoluminescence is dependent on the silical hydroxide concentration, and the change is apparently autocatalytic. Both chemi- and photo-luminescence are strengthened in liquid air, although the velocity of reaction is reduced. The substances in liquid air also exhibit phosphorescence with the same colour as that of the chemiluminescence. The emitted light is plane polarised. W. E. G.

**The Theory of Klein and Rosseland applied to Fluorescence, Photochemical Processes, and the Electron emission from Hot Substances.** J. FRANCK (*Z. Physik*, 1922, **9**, 259—266).—The theory proposed by Klein and Rosseland (cf. 1921, ii, 291) is of [illegible]nded to collisions between atoms and molecules. It is with[illegible]t to determine the percentage of excited molecules which

ndergo a change from the active into the normal condition after ɔllision *with a slow unexcited atom*. The fluorescence of dilute ɩdine gas is shifted towards the red end of the spectrum by the ddition of another gas. This result suggests that some of the xcited molecules may transfer their rotation and vibration quanta ɔ the colliding atoms without the emission of light. Observations f Wood and of the author on the resonance spectrum of the ɩercury line 2536·7 lead to the conclusion that the number of ɩyless transformations in the collision of excited atoms with slow ɩoving atoms is not small compared with unity. In solids at ɩgh temperatures, the number of rayless quantum changes with beration of electrons is large compared with the number of quantum ɩanges taking place with the emission of light. W. E. G.

**Photocatalysis. II. The Photosynthesis of Nitrogen Compounds from Nitrates and Carbon Dioxide.** EDWARD HARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and DONALD RYCE HUDSON (T., 1922, **121**, 1078—1088).

**Photochemical Activity of the Triphenylmethanesulhonic Acids.** EDWARD O. HOLMES, jun. (*J. Amer. Chem. Soc.*, ɔ22, **44**, 1002—1008).—Solutions of magenta, malachite-green, ethyl-violet, and crystal-violet which have been decolorised by ɩlphur dioxide when exposed to ultra-violet light of wave-length ɜtween 2200 Å.U. and 3300 Å.U. develop their original colours. ɔmparison of the absorption spectra of the original dyes and ɩose which had regained the colour showed that the regained ɔlour is due to the original dye, since the absorption spectrum the same in both cases. It is shown that the reaction with ɩphurous acid is reversible and consists of a decolorising action ɩd a colorising action, the latter of which is photochemical. The rge quanta of energy supplied by the ultra-violet light cause e photochemical action to increase and consequently a disacement of the position of equilibrium occurs. The equilibrium ɔsition can also be displaced by chemical and thermal means.

J. F. S.

**A Determination of the Number of α-Particles per Second mitted by Thorium-*C* of known γ-Ray Activity.** ALLEN . SHENSTONE and HERMAN SCHLUNDT (*Phil. Mag.*, 1922, [vi], ɜ, 1038—1047).—A direct comparison is made between the ɩmber of α-particles and the γ-ray activities of radium-*C* and orium-*C*. α-Particles of ranges 8·6 cm. (thorium-*C*) and 6·96 cm. adium-*C*) were counted by the wheel method devised by Rutherrd, and accurate γ-ray measurements were made at the same ne as the counts. The ratio αTh-*C*/αRa-*C* for equal γ-ray tivities is not independent of the thickness of the wall of the ray electroscope. Values of this ratio have been determined for icknesses of lead ranging from 3·3 to 14·3 mm. For 3·3 mm., e ratio = 0·75. The γ-ray activities of thorium-*C*, radium-*C*, ɩd a radium standard are given for the same range of thicknesses lead. W. E. G.

**The Interpretation of $\beta$-Ray and $\gamma$-Ray Spectra.** C. ] Ellis (*Proc. Camb. Phil. Soc.*, 1922, **21**, 121—128).—The research of Rutherford and Chadwick have shown that the β-rays from radioactive atom may be separated into a general and a magnet line spectrum. The latter (cf. this vol., ii, 339) may be account for, if the γ-rays are the primary phenomena in the disintegratio of the atom. The details of five different β-ray spectra (radium-. radium-*C*, radium-*D*, thorium-*B*, thorium-*D*) lend support to th theory. The γ-rays are emitted during the movement of a electron from one stationary state in the nucleus to another. Son of these rays are absorbed in the electronic structure of the san atom and eject electrons with characteristic energies from th *K*, *L*, and *M* levels. When an electron arrives in a stationar state, in which it is not permanently stable, it is ejected from th nucleus. This electron, which has a variable kinetic energy, giv rise to the continuous or general spectrum. The numerical resul obtained in this paper do not support the theory of Meitner (th vol., ii, 416), which affirms that the emission of a β-particle is th primary phenomenon in the disintegration of the atom.

W. E. G.

**The Chemical Action of Penetrating Radium Rays. XIII The Velocity of Formation and Equilibrium of Hydroge Peroxide.** Anton Kailan (*Monatsh.*, 1921, **42**, 387—398).— It is known that penetrating radium rays accelerate both th formation and decomposition of hydrogen peroxide (cf. A., 1912 ii, 10). Experiments have now been made to determine th equilibrium concentration of hydrogen peroxide in neutral solutio and in solutions of varying degrees of acidity, since the stabilit of hydrogen peroxide is known to depend on the hydrogen-io concentration. Experiments were made using the same sample of radium as in the previous work, at temperatures from 6° to 13' No difference was found between Merck's perhydrol and ordinar hydrogen peroxide. At equilibrium the concentration of hydroge peroxide, in gram equivalents per litre, was 0·005 and 0·001 whe the hydrogen-ion concentration was 0·5 and 0·008 gram-ion pe litre, respectively, whilst in neutral solution the equilibrium con centration was only 0·0006. Impurities present in ordinary dis tilled water lowered the equilibrium concentration in acid solution The reaction velocity in either direction agrees with the equatio $k=1/t \log a-b/a-b-y$, where $b$ is the concentration at equilibrium $a$ the original concentration and $a-y$ the concentration after time $t$ The values of $k$ found at hydrogen-ion concentrations $10^{-7}$, 0·008 and 0·5 were $7\times10^{-3}$, $0{\cdot}7\times10^{-3}$, and $0{\cdot}14\times10^{-3}$, respectively. Th higher equilibrium concentration in acid solutions than in neutra solutions is due mainly to the retardation of decomposition o hydrogen peroxide in acid solution. It is calculated that for eacl primary β-particle, in neutral solution $3{\cdot}10^3$ and in acid solution from 0·1 to 1·0*N*, $6{\cdot}10^3$ molecules of hydrogen peroxide are forme per second. A discrepancy between the velocity of formatio 'nd now and in 1911—1912 (*loc. cit.*) is discussed at length

it may be due to physical changes in the glass apparatus brought about by prolonged exposure to radium rays.

The number of molecules of hydrogen peroxide formed is of the same order as the number of ion pairs from the total absorbed rays. This supports the view that there is a relation between ionisation and chemical action for β- and γ-rays as well as for α-rays. On the other hand, the ratio of hydrogen peroxide molecules decomposed to number of ion pairs is 1500 : 1 and the mechanism of decomposition appears to be different from that of formation. Some experiments on the decomposition of hydrogen peroxide in the light of a quartz mercury vapour lamp are also recorded. The velocity coefficient is much greater than with radium rays. E. H. R.

**Electrical Charges of Colloidal Particles and Anomalous Osmosis. II. Influence of the Radius of the Ion.** Jacques Loeb (*J. gen. Physiol.*, 1922, **4**, 621—627; cf. this vol., ii, 354).—The rate of transport of water and the potential difference across a collodion–gelatin membrane separating solutions of the chlorides of potassium, sodium, and lithium from pure water, when the $P_H$ is on the acid side of the isoelectric point of gelatin, vary inversely with the radius of the kations. At $P_H$ 3·0 the influence of the three salts on the potential difference between the liquid and the membrane inside the pores of the gelatin is identical. The influence of the three salts on the potential difference across the membrane varies inversely as the relative mobilities of the kations, which suggests that this influence may be due to a diffusion potential. C. R. H.

**Effect of Hydrogen Pressure on the Electromotive Force of a Hydrogen–Calomel Cell. I.** William R. Hainsworth and Duncan A. MacInnes (*J. Amer. Chem. Soc.*, 1922, **44**, 1021—1032).—The effect of pressure of hydrogen on the cell $H_2|HCl(0{\cdot}1N)HgCl|Hg$ has been investigated at 25° for pressures up to 400 atmospheres, and the change of *E.M.F.* by pressure calculated. The thermodynamic theory of the change of *E.M.F.* has been investigated and the expression $\Delta E=0{\cdot}02958 \log p+6{\cdot}56\times10^{-6}(p-1)+3{\cdot}7\times10^{-10}(p^2-1)$ obtained for the change of *E.M.F.* The calculated and the observed values have been compared and are as follows: 50 atmos. $\Delta E=0{\cdot}0504$ volt (0·0506), 100 atmos. $\Delta E=0{\cdot}0594$ (0·0598), 200 atmos. $\Delta E=0{\cdot}0688$ (0·0694), 300 atmos. $\Delta E=0{\cdot}0745$ (0·0753), and 400 atmos. $\Delta E=0{\cdot}0787$ (0·0797). The values in brackets are the calculated values. The values indicate that the thermodynamic theory as developed does not quite represent the measurements at higher pressures. This is probably due to the solubility of hydrogen, and it would appear that a correction to account for the solubility must be introduced. J. F. S.

**Carbon Monoxide–Oxygen Cell with Glass as Electrolyte.** Hartmut Kallmann (*Z. Elektrochem.*, 1922, **28**, 81—85).—The *E.M.F.* of cells containing mixtures of carbon monoxide, carbon dioxide, and oxygen on one side of a glass wall and air on the other

side has been determined at 717° under various pressures fr( 920—800 mm. It is shown that the *E.M.F.* for such a cell expressed by the equation $E=1{\cdot}118-0{\cdot}0707 \log p_{CO_2}/p_{CO}\cdot p_{O_2}^{1/2}$. T experimental values agree with the values calculated by the equati to within 0·9%. J. F. S.

**Use of Phthalate Solutions for Hydrogen Electro Standards.** EARLE T. OAKES and HENRY M. SALISBURY ( *Amer. Chem. Soc.*, 1922, **44**, 948—951).—The proposal recent made to replace the calomel electrode as a standard of *E.M.* measurement by a hydrogen electrode made up in alkaline solutio of phthalates has been investigated; and it is found that wh such a phthalate solution, of $P_H$ value 6·0 as measured by indicato is measured against a calomel electrode, the *E.M.F.* slowly dri in forty-eight and a half hours from about 0·57 to 0·66, that to a $P_H$ value of 7·01. This change in the $P_H$ value was confirm by indicators. It is held that the change in the $P_H$ value is d to a change in the phthalate itself, probably a reduction, and n to reduction of impurities, for the purification had been such to exclude the large quantities of impurities necessary to bri about the observed change. If impurities are responsible for t change in *E.M.F.* their action must be that of catalysts reduci the phthalate. Hence, unless specially pure, phthalate solutio are unsuitable as standards for measuring hydrogen-ion conce trations. J. F. S.

**Instability of Phthalate Potentials.** WM. MANSFIELD CLAR (*J. Amer. Chem. Soc.*, 1922, **44**, 1072—1073; cf. preceding abstract —The author has re-examined some phthalate hydrogen electrode over a period of twenty-four hours and has been unable to find drift of more than 1·0 millivolt, and in the last fifteen hours of th observation the drift was less than 0·00005 volt. There was als no change in the Sörensen value. The author is therefore unabl to explain the very large changes observed by Oakes and Salisbur (*loc. cit.*). J. F. S.

**New Conceptions of Electrolytes. III. The Hydratio of the Hydrogen Ion.** ERLING SCHREINER (*Z. anorg. Chem.* 1922, **121**, 321—334; cf. A., 1921, ii, 425, 498).—The autho measured the *E.M.F.* of the hydrogen ion in 0·001, 0·002, and 0·00 molar hydrochloric acid in potassium chloride solutions the concentration of which varied from 0·001 to 3·0 molar. The quinhydrone electrode was employed (cf. Biilmann, A., 1921, ii, 372). These measurements do not give the concentration of hydrogen ions, but the activity of these ions which is associated only with the non-hydrated ions. The author has given the method of calculation in a previous communication (A., 1921, ii, 425). The results obtained were fairly constant and showed that 8—9 molecules of water are on an average associated with each hydrogen ion, a result in good agreement with that found by Bjerrum (*Z. anorg. Chem.*, 1920, **109**, 275). W. T.

**Electrochemical Oxidation of Organic Compounds.** RICH MÜLLER (*Z. Elektrochem.*, 1922, **28**, 101—106).—A theotical paper in which the author discusses the views put forward y Fichter (this vol., ii, 23) and makes his own views clear. It is own that the assertion of Fichter, that his views on electroemical oxidation and those of the author are in agreement, is ot true. Whilst the author assumes the discharge of anions, ichter supports the view of a primary formation of oxygen and e accompanying purely chemical oxidation. Fichter assumes e intermediate formation of peroxides or peracids, the method formation and decomposition of which is not explained, and nsequently furnishes nothing toward the explanation of electroemical processes. Such per-compounds may be prepared chemicly, but their decomposition is to some extent different from what ould be expected from the view that they are formed at the anode d from the products of electrolysis. The author accepts the rmation of intermediate hydroxy-compounds, formed by the ischarge of anions, which decompose in a manner in keeping with cts, and present a mechanism for both the chemical and electroemical oxidation. The view of Fichter that the substitution of ischarge processes at the anode by purely chemical oxidations ontributes to the understanding of the course of electrolytic xidations is incorrect. J. F. S.

**Magnetic Properties and Atomic Structure.** B. CABRERA *Anal. Fís. Quím.*, 1922, **20**, 92—97).—A theoretical discussion of e relation between magnetic properties and atomic structure in e metals of the iron group. It is suggested that the *N*-electrons ay be divided into two concentric subdivisions, the more supercial, $N_2$, being the valency electrons and those beneath, $N_1$, hose with which magnetic properties are associated. It is supposed that the relation between magnetic moment and the number f $N_1$ electrons is periodic. The magnetic moment reaches a aximum for bivalent magnanese and tervalent iron with five $N_1$-electrons and diminishes to zero with increasing number of $N_1$-electrons. G. W. R.

**Magnetism and Atomic Structure. II. The Constitution of the Hydrogen–Palladium System and other Similar Systems.** A. E. OXLEY (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 264—79; cf. A., 1921, ii, 82).—The specific magnetic susceptibility of alladium black, the value of which is $+64{\cdot}6\times10^{-7}$, is considerably educed by occluded hydrogen, the greatest reduction observed eing about 75% to $+14{\cdot}7\times10^{-7}$ when great care was taken to revent loss of hydrogen after charging. The specific susceptibility radually returns to its original value as the occluded hydrogen scapes. If the occluded hydrogen were in the atomic state, it vould be expected to increase the specific susceptibility. On the ther hand, molecular hydrogen, liquid or gaseous, being dianagnetic, should reduce the specific susceptibility by a calculable mount. The maximum reduction on this assumption would be $\cdot19\times10^{-7}$, an amount insufficient to account for the observed

reduction. The experimental results may be accounted for on the assumption that a loose compound is formed, possibly having the composition $Pd_2H$. That the presence of such a loose compound should lower the magnetic susceptibility is not surprising when it is remembered that the carbonyls of iron and of nickel are both diamagnetic. It is noteworthy that a loose compound of the composition PdH would form a system of two nuclei with an electronic system resembling that of silver, the atomic number of which exceeds that of palladium by one. Such a system would be expected to have a magnetic susceptibility very nearly equal to that of silver, $-1{\cdot}8\times10^{-7}$. If half the palladium atoms were in this form, its susceptibility would be reduced by about 50%. The difference between the occluding powers of amorphous and crystalline palladium is discussed. The slow diffusion of hydrogen into crystalline palladium can be understood when its face-centred cubic lattice is taken into account.

When manganese is fused in an atmosphere of hydrogen, or is deposited electrolytically, it becomes ferromagnetic with a specific susceptibility $+2000\times10^{-6}$, its normal value being $+11{\cdot}0\times10^{-6}$. It may be supposed that the presence of hydrogen produces with the manganese, atomic number 25, a certain number of electron systems similar to that of iron, atomic number 26, and that these are the cause of the observed ferromagnetic properties. This suggestion is discussed in connexion with the Lewis-Langmuir theory. E. H. R.

**Determination of High Temperatures by Effusion of Gases.** YOHEI YAMAGUCHI (*J. Chem. Soc. Japan*, 1922, **43**, 1—21).—The author has studied the relations between pressure and temperature on the passage of a gas through a capillary tube of quartz. (1) The increase of pressure necessary to pass the same quantity of air through a quartz capillary tube at various temperatures was investigated. A linear relation, $\log p=a\log T+b$, holds between the pressure ($p$) and the absolute temperature ($T$) within the range 17° to 1205°. This, however, cannot be applied to the measurement of temperature, owing to the complexity of the apparatus necessary, and the difficulty of regulating the pressure. (2) Using the same capillary, the relation between the effluent velocity of the transpired air and its temperature has been investigated, no simple linear relation being found for the temperature interval 20·5° to 1046°. (3) The relation was investigated between temperature and the effluent velocity of air as measured by its effusion through a small hole in the round bottom of a quartz tube. A linear relation, $t=a+b\sqrt{T}$, holds between the effluent time ($t$) and the absolute temperature ($T$) of the tube heated by an electric furnace at temperatures from 17° to 1125° which can be applied to the measurement of high temperatures. K. K.

**Considerations on Cooling and Heating Curves.** R. ARIANO (*Gazzetta*, 1922, **52**, i, 246—261).—The author considers the courses followed normally, that is, when no transformation occurs, during

cooling or heating, by: (1) the temperature–time curve, and (2) the curve representing the difference between the temperature of the substance examined, $T$, and that of a second substance, chosen for comparison, $T_1$, as a function of the latter temperature, $T-T_1=f(T_1)$.

As regards the temperature–time curve, it is first shown theoretically that Newton's law expresses, without appreciable error, the transference of heat between furnace and sample in the case of the cooling of metallic samples of small dimensions. Analogous reasoning applies in the case of heating curves. Cooling curves are exponential in form and are defined by equations of the type $T=k+Ae^{-a\theta/Pc}$, whilst heating curves are probably represented by equations of the form $T=k+Ae^{-a\theta/Pc}+f(\theta)$, $\theta$ being the time, $a$ the product of the coefficient of external thermal conductivity and the surface, $P$ the weight of the sample, and $c$ its mean specific heat. The results of cooling and heating experiments with silver show that $A$ in the former of the two above equations is sensibly identical with the temperature at the beginning of the cooling ($t_1$), $k$ being consequently nearly zero in magnitude.

As regards the differential curve, $T-T_1=f(T_1)$, it is shown theoretically and confirmed experimentally that, if the sample chosen for comparison undergoes no transformation in the interval of temperature chosen, this curve exhibits a maximum almost at the beginning of the cooling. In order that the normal course of the curve may be as nearly rectilinear as possible, the specific heats of the two samples and their mode of variation with temperature should be almost coincident; the same should hold for the values of the ratio, weight : surface, for the coefficients of linear expansion and their variation with temperature, and for the coefficients of external conductivity. T. H. P.

**Revision of the Entropies of the Elements.** GILBERT N. LEWIS and W. M. LATIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1008—1017).—A theoretical paper in which on the basis of new determinations of the specific heats of many elements the entropy has been recalculated. By means of the equation $S=3/2R\log_e W+25{\cdot}70$ the entropies of nitrogen, oxygen, fluorine, sodium, chlorine, potassium, calcium, zinc, bromine, cadmium, iodine, cæsium, and mercury have been calculated in the state of monatomic gas. In four cases where the experimental values are of sufficient accuracy a comparison is made between the experimental values and the calculated values for 25° and 1 atmos. The following are recorded where the values in brackets are those calculated: helium 29·2 (29·8), argon 36·4 (36·7), cadmium 40·0 (39·8), and mercury 41·3 (41·5). A table of entropies at 1 atm. and 25° has been drawn up and is appended to the paper. J. F. S.

**Electrically Heated Apparatus for the Determination of Melting Points.** UYTENBOGAART, jun. (*Chem. Ztg.*, 1922, **46**, 493).—The apparatus consists of a circular glass tube at the bottom of which a platinum resistance is placed; it is filled with water, glycerol, or sulphuric acid ($d$ 1·84). The liquid, warmed by the

platinum resistance, rises uniformly in the two limbs and the currents, joining at the top, pass down a central tube which contains the thermometer and substance, with a kind of whirlpool motion. For temperatures up to 75°, an ordinary 4-volt accumulator is sufficiently powerful, but for higher temperatures it is preferable to use the lighting current with a suitable resistance in the circuit. H. W.

**Binary Liquid Mixtures.** GERHARD C. SCHMIDT (*Z. physikal Chem.*, 1922, **101**, 286—291).—An answer to the criticisms of Faust (this vol., ii, 423), Cassel (this vol., ii, 424), and Schulze (this vol. ii, 424) on the views expressed by the author in connexion with Dolezalek's theory of binary liquid mixtures (this vol., ii, 119). J. F. S.

**Heat of Vaporisation and the Difference, *m′-m*, of the Specific Heats at the State of Saturation for Argon, Oxygen, Nitrogen, and Hydrogen.** E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1922, **174**, 1395—1397; cf. A., 1921, ii, 256).—A mathematical paper in which formulæ are given for the four gases by means of which it is possible to calculate the latent heat and hence the reduced heat of vaporisation, and also the difference between the specific heats of the saturated vapour and the saturated liquid. W. G.

**The Vapour Pressure of Hydrogen and New Thermometric determinations in the Domain of Liquid Hydrogen.** J. PALACIOS MARTINEZ and H. KAMERLINGH ONNES (*Arch. Néerland*, 1922, [iii], **6**, 31—39).—Cath and Onnes (A., 1918, ii, 218) could not explain the disagreement of their results for the vapour pressure of hydrogen in the neighbourhood of its boiling point with the values found by Keesom and Onnes. The former authors determined the temperatures directly by means of a helium thermometer, whilst the latter employed a platinum resistance thermometer, the values obtained being reduced to the hydrogen and helium thermometers by Onnes and Holst. The present authors redetermined these measurements between the absolute temperatures 14·10° and 20·63°, particular attention being directed to the boiling point of hydrogen, an important point on the temperature scale. The boiling point was found to be 20·35°, a value agreeing with that found by Keesom and Onnes; for points immediately below the boiling point the results agreed with those of Cath and Onnes. All the results are given in a table. The calibration of platinum thermometers is also described. W. T.

**The Distillation of Greatly Frothing Liquids.** KLÄNHARDT (*Chem. Ztg.*, 1922, **46**, 493).—The difficulty in effecting the distillation of foaming liquids, such as aqueous solutions of soap or saponins, can be easily overcome by passing a current of compressed gas (such as carbon dioxide) over the surface of the liquid. A suitable apparatus for the introduction of the gas is a tube terminating in a ball of 2 cm. diameter in which three series of holes about

1 mm. in diameter are blown. Distillations with steam can also be smoothly effected in this manner. H. W.

**Maintenance of the Adiabatic Condition in Calorimetry.** FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1922, **44**, 899—937; cf. *A.*, 1920, ii, 734).—An extensive series of measurements is described, which were undertaken to establish a standard of accuracy for the calorimetry of slow processes. It is shown that to attain the accuracy defined by the loss or gain of 0·5 gram-calorie in ten hours, the following precautions are necessary and sufficient. A closed calorimetric system must be used which allows no measurable evaporation into the insulating air gaps, and these gaps must be dry. The outer environment must be thermostatically controlled, whenever there are conducting parts which pass directly from the calorimeter to the surrounding air, with a precision characteristic of the system employed. This is about $\pm 0{\cdot}2°$ when encased mercury thermometers are used. It is always advisable to keep the environmental temperature close to the calorimetric within the characteristic range of negligible direct leakage; and it is necessary to correct for fluctuation beyond this range. For this control, a constant temperature chamber is essential. A convenient structure for this purpose is described. With the usual system of about 1000 cal. heat capacity the air gaps should not be less than 40 mm. wide and there is no advantage in larger gaps. With a 40 mm. gap, when the temperature fluctuates within $\pm 0{\cdot}01°$ and the environment within 0·2° of the calorimetric temperature, the system is practically adiabatic within the error defined above, the total leakage being little more than three times that of a perfect vacuum gap. The leakage rate in such systems is the same in both directions and for heads below 0·1° is proportional to the head. Corrections for imperfect adiabaticity due to bath fluctuation may be made on this basis, since transmission lag has no measurable effect on the leakage. A calorimeter based on the above-named conditions is described. With this calorimeter, the initial conditions are perfectly adiabatic; and the total calorimetric lag for the temperature changes characteristic of long-continued operations is negligible. It is permissible and advantageous to stir the closed system reciprocally. In the system described, this may be done without significant loss of heat. The heat of stirring is developed identically in different assemblages and at the same rate for any one speed, whether stirring is intermittent or continuous. It may vary at low speeds with the fourth and higher powers of the speed. The continuous stirring necessary to ensure mixture in chemically reacting systems is productive of negligible error; and similar stirring at low speeds throughout determinations is shown to be practicable, although in very protracted operations intermittent stirring is better. Strictly uniform speeds are necessary for long, continuous stirring, but not for intermittent stirring, nor for continuous stirring during mixture if the approximate rates of heat production under different speeds be known for the system used. The open calorimeter is unavailable in protracted calori-

metry, since, even with an initially dry gap, evaporation leakage is inconstant as the result of uncontrollable variability in prior conditions. This is due in great part to the condensation of water vapour in the air gap on the walls of the calorimeter, which occurs on clean as well as on dirty surfaces, and is probably due to the simple adsorption of moisture, an effect which can be neither eliminated nor controlled even under approximately isothermal conditions. With change of temperature, its effects are greater and still more irregular, and in gaps saturated with water are complicated in the extreme. The close system is best for all types of calorimetry; but in the adiabatic measurement of swift reactions the open calorimeter may be safely used, either with dry surfaces in an initially dry gap, or with invisibly wetted surfaces in a saturated gap which holds no water, provided always that correction for aggregate thermal disturbances due to evaporation leakage be made by interpolation from the results of observations taken before and after the reaction period. The initially dry gap, with which leakage is less and more nearly uniform, is preferable in such measurements; but correction for imperfect adiabaticity is safer with the saturated gap. Under all heads less than 1°, the total leakage from a closed calorimeter system in a dry gap shows slight divergence from Newton's law, since the convection increases very slowly with increase in gap width, and varies as powers of the thermal head less than two except when the gap is unusually wide. Similar leakage from the open system is irregular, but yields itself to a rough analysis which gives some indication of the character of the thermal disturbances and the magnitude of the uncertainties characteristic of the merodiabatic measurements which have yielded the bulk of the present thermochemical data. J. F. S.

**Calorimetric Researches: (I) The Standardisation of a Calorimetric System; Comparison of the Heats of Combustion of the Substances Used for Standardisation: Benzoic Acid and Naphthalene.** P. E. Verkade, J. Coops, jun., and H. Hartman (*Rec. trav. chim.*, 1922, **41**, 241—277).—A discussion of previous work on this subject and its bearing on the authors' experiments. Standardisation of the apparatus was effected as the result of thirty-seven experiments in the combustion of benzoic acid and thirty-six in the combustion of naphthalene. A detailed description is given of the apparatus used, the method of carrying out the experiments and the corrections applied to the results. Adiabatic calorimetry was discarded in favour of the ordinary methods for various reasons; there is little difference in the results obtained by the two methods (cf. Dickinson, A., 1914, ii, 802, and Swientoslawski, A., 1921, ii, 679). The ratio between the values obtained for the two substances used agrees with that of Dickinson, the figure given by Swientoslawski (A., 1918, ii, 32) is criticised on both theoretical and practical grounds. In order to carry out an absolute standardisation of a calorimetric system, a standard substance should be chosen the heat of combustion of which is known with the greatest possible accuracy. The results obtained

by the authors show that benzoic acid should be preferred to naphthalene, as it gives more constant results, is easily obtained pure, and is practically non-hygroscopic. Naphthalene, on the other hand, does not undergo complete combustion in many experiments, and also loses weight by evaporation; figures are given in illustration of the latter objection. Other substances suggested for the purpose are not so easily obtained pure as is benzoic acid. The value finally recommended as the standard ratio of the heats of combustion of naphthalene and benzoic acid is 1·5203. H. J. E.

**Heat of Combustion of Lactic Acid.** OTTO MEYERHOF (*Biochem. Z.*, 1922, **129**, 594—604).—The author has determined the heat of combustion of lactic acid (in dilute aqueous solution) from the heat of combustion of zinc lactate, the heat of dilution of lactic acid, the heat of neutralisation of zinc oxide and lactic acid, and the heat of solution of zinc lactate in water. The value found for 1 gram of lactic acid is 3615 cal. H. K.

**Heat of Solution of Zinc in Hydrochloric Acid.** THEODORE W. RICHARDS and THORBERGUR THORVALDSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1051—1060).—A new apparatus is described, suitable for dissolving substances in a comparatively small excess of liquid and providing a conveniently large heat capacity for the reception of the heat. With this apparatus the heat of the reaction $Zn+2(HCl,200H_2O)=ZnCl_2,400H_2O+H_2$ was found to be 36·32 Cal. (or 151·8 kilojoules) if the hydrogen is dry, and 36·07 Cal. (or 150·8 kilojoules) if the hydrogen is moist at 20°. The total energy change, *U*, of this reaction is therefore 36·90 Cal. (or 154·2 kilojoules) at 20°. The heats of dilution of factors and products needed for the calculation of the above results were determined experimentally. The temperature-coefficient of the heat of solution of zinc in concentrated hydrochloric acid is shown to be negative and of considerable magnitude; even with diluted acid it probably amounts to −30 cal. per degree. J. F. S.

**Heat of Solution of Cadmium in Hydrochloric Acid.** THEODORE W. RICHARDS and SETSURO TAMARU (*J. Amer. Chem. Soc.*, 1922, **44**, 1060—1066).—Using the apparatus previously described (cf. preceding abstract), the heat of the reaction $Cd+2(HCl,200H_2O)=CdCl_2,400H_2O+(H_2)_p$ is found to be 17·23 Cal. (or 72·0 kilojoules) at 20° if the hydrogen is dry, and 16·98 Cal. (or 71·0 kilojoules) if the hydrogen is moist at 20° and 760 mm. The total energy change, *U*, of the reaction is therefore 17·81 Cal. (or 74·4 kilojoules) at 20°. The temperature-coefficient of the heat of solution of cadmium in concentrated hydrochloric acid is shown to be negative −71 cal. per degree, and probably with diluted acid it amounts to −30 cal. per degree. All the necessary factors used in the present calculation were determined experimentally. J. F. S.

**Heat of Transformation of Austenite into Martensite and of Martensite into Pearlite.** NOBUO YAMADA (*Sci. Rep. Tohoku Imp. Univ.*, 1922, **10**, 453—470).—The heat of dissolution of carbon

in iron and also the heat content of austenite and pearlite a determined in a series of carbon steels ranging from 0·38—1·74 carbon. The heat of dissolution of carbon in iron is shown be a linear function of the carbon content of the steel and amour to 1130 cal. per gram of carbon. By combining the results obtain with those of Meuthen (cf. A., 1913, ii, 385) for the total heat transformation, the heat of allotropic transformation of austeni to martensite is calculated. It is a linear function of the carb content and has a maximum value of 5·6 cal. per gram for eutect steel. For a carbon content of 0·38% carbon, the value is 2·4 ca and for 1·74% carbon 4·8 cal. Martensite has a definite heat conte corresponding with the quantity of dissolved carbon, a defini crystalline form stable at ordinary temperatures, characterist physical properties as compared with austenite or pearlite, ar must therefore be considered as an independent phase. It shown that troostite, sorbite, and pearlite have the same speci heats within the limits of experimental error. It is confirmed th the transformation of austenite into pearlite involves the inte mediate production of martensite. J. B. F.

**Some Remarkable Properties of Gases.** FRIEDRIC WÄCHTER (*Z. anorg. Chem.*, 1922, **121**, 225—239).—A theoretic paper which derives from Naumann's formula the lowest valu for the molecular weight of gases to enable them to remain in th atmosphere of a planet. Hydrogen can exist in our atmospher but not in the atmosphere of the moon. In the atmosphere the sun, a gas with a molecular weight 1/1864 can remain. Th author identifies these imponderable molecules with the light ethe which he thus regards as a very light gas susceptible to the Loren contraction. He concludes from the above that the apparen mass of electrons as found by Kaufmann and Bucherer is merel a proof of the Lorenz contraction in the ether; thus the idea apparent mass in the interior of the atom is not justified. Instea of the idea of β-particles or atoms of electricity, the author sugges the atoms of the lightest ponderable gas of invariable mass, an on this hypothesis finds that the enormous velocities in the inn atom such as Bohr calculated for the Rutherford atom are unnece sary. These results are also applied to the radioactive atoms. A earlier paper dealt with the astronomical implications, such as th Michelson's experiment, the abnormal motion of mercury, and th displacement of spectral lines (*Astron. Z.*, 1921, **4**, 62). W. T.

**Specific Characters of Hydrolytic Decomposition.** S. T. TROMP (*Rec. trav. chim.*, 1922, **41**, 278—295; cf. Schoorl, A 1920, i, 531).—A study of the specific volume occupied by th molecule of water which is fixed in various reactions. An exami ation of esters, cyanides, carbylamines, nitro-compounds, anhydride ethers, oximes, amides, and acetals shows that the volume of th water taken up varies little in one type of reaction, but conside ably from one type to another. This method of investigatio shows that neither cyanides nor carbylamines should be regarde as esters of hydrocyanic acid and also provides a means of di

tinguishing between nitrites and nitro-compounds, also between cyanides and carbylamines. The values obtained for anisole and phenetole show that these substances are esters of phenol rather than ethers, and the view of saccharose as an ether is corroborated. Comparison of the specific refraction of fixed water with that of water as such gives no such trustworthy data as the discrepancies are considerable and numerous. H. J. E.

**Thin Films of Binary Mixtures (Glycerides).** (MLLE) PAULE COLLET (*J. Phys. Radium*, 1922, [vi], **3**, 128—132).—Mixtures of various glycerides in benzene solution are applied to the surface of water and determinations made of the surface covered. No additive relationships were found for binary mixtures, the curves always showing either maxima or minima. These maxima and minima appear to correspond with changes of physical state and with a simple ratio of the number of molecules of the two constituents. On the assumptions that all the molecules are associated at the maximum and minimum value of the area covered and that the free molecules of the glycerides cannot exist side by side, it is possible to derive theoretical curves which are in good agreement with the experimental results. W. E. G.

**Examination of the Compression Equation of Liquids by means of the Data of Amagat and Bridgman.** H. CARL (*Z. physikal. Chem.*, 1922, **101**, 238—268).—The compression equation put forward by Wohl (this vol., ii, 117) which has the form $e^{(v_0-v)/A}=1+(p-p_0)/(k+p_0)$; $v_0\alpha=A$; $k=b\tau-c$ has been tested by means of Amagat and Bridgman's isothermals for twelve liquids. In the expression, $K$ is a pressure quantity for the internal pressure of liquids and $\alpha$ a constant, which expresses the influence of different initial resistances and the distances of molecules and atoms in the liquid. Every normal liquid has a constant $\alpha$ value over the whole temperature range 0—80°, and the $K$ value in the limit is sufficient *in the case of normal liquids for rising temperature in the above* equation. Water exhibits here the known anomaly in its volume change up to pressures of 2500 kg./cm.$^2$ At 50°, it shows first a regular behaviour with increasing temperature. The constant $\alpha$ is constant over the whole range of temperature, but the $K$ values cannot, as is to be expected from the foregoing, be brought into a linear equation, since from 50° downwards $K$ decreases with increasing temperature. Similar anomalies are shown by ethyl alcohol for lower pressures, according to Amagat's data for 1—1000 atmos., $\alpha$ is not constant over the temperature range 0—180°, and $K$ does not decrease so regularly with increasing temperature, as is shown to be the case for all normal liquids. The agreement between the $v$ value calculated by the above equations and those from Amagat's isothermals is excellent. A mean divergence of 0—2 units is found in the last place of decimals, the error of experiment being 6 units. Larger divergences have been shown from a series of differences to be due to experimental errors. In the case of Bridgman's results for higher pressures, the agreement has a mean divergence of 0·5%. A reduced form of the equation, in

which the pressure values are expressed as fractions of $p_k$, ha been obtained. By inserting $K/p_k=b\tau/p_k-c/p_k=1/\beta(\tau-\gamma)$ th equation $(v_0-v)/v_0=\alpha\log_e[1+\beta(\pi-\pi_0)/(\tau-\gamma-\pi_0/\beta)]$ is obtaine and on placing $p_0=0$ in this the simplified form $(v_0-v)/v_0=$ $\alpha\log_e[1+\beta\pi/(\tau-\gamma)]$ results. A table containing the values $\alpha$, $\beta$, and $\gamma$ and the critical data of the substances examined included in the paper. J. F. S.

**Negative Viscosity.** ADOLPH I. RABINOVICH (*J. Amer. Chem Soc.*, 1922, **44**, 954—964).—The term negative viscosity is applie to the viscosity of solutions which have lower viscosities than th solvents. With the object of explaining negative viscosity, th author discusses a large number of factors which may determin the viscosity of solutions. The factors considered are, (*a*) viscosit of the solvent, (*b*) viscosity of the solute, (*c*) solvation, (*d*) formatio of complex ions and molecules, (*e*) the electric fields of the ion (*f*) depolymerisation of associated solvents, (*g*) electrostrictio and (*h*) depolymerisation of the solute. J. F. S.

**Significance of Surface Tension Phenomena for the Dair Practice.** OTTO RAHN (*Kolloid Z.*, 1922, **30**, 341—346).—Th author has studied the formation of the foam which accompanie the pouring of skim milk from the cream separator. It is show that foaming is due to a reduction of the surface tension cause by the accumulation in the surface of an albuminous substanc which passes into the walls of the foam. These walls are show to contain a solid substance, and the drying of such material i shown to be similar to the drying of many albuminous substance inasmuch as it is irreversible. It is probable that this soli albuminoid is the main constituent of the skin which forms on th surface of milk which has been heated at 60° or above. On th basis of the foregoing, the formation of whipped cream is explaine as follows: on whipping cream a network of foam is produce which is stiffened by the solidified fat so that it does not fall lik the foam but retains its form. A microscopic examination o whipped cream shows that it consists of a solid structure of albumi penetrated by layers of solid fat which has the same form as th foam. On warming whipped cream above the melting point o the fat, the structure collapses, but remains somewhat froth because the albumin cannot melt. Butter formation is explaine as follows: The cream contains much of the foam producin albumin; this surrounds the particles of fat. On churning, a larg volume of air is entrapped by the cream, so that the surface is ver much enlarged. The albumin passes into the walls of the foa and takes the fat with it, so that a foam rich in fat stands above liquid poor in fat (buttermilk). The fat particles lie very clos together in the foam walls and are compressed by the surfac pressure to form conglomerates of fat particles. This causes th albumin in the walls to solidify and further churning breaks u the foam and mixes the fat conglomerates with the solid albumi to form lumps of butter. It is shown that butter may be formed a 34°, but not at 39°. J. F. S.

**Theory of Adsorption Processes.** M. POLANYI (*Z. Elektrochem.*, 1922, **28**, 110—111).—A criticism of Eucken's paper (this vol., ii, 262) on the theory of adsorption processes. J. F. S.

**The Adsorption Problem. Sorption of Vapours by Charcoal.** BROR GUSTAVER (*Koll. Chem. Beihefte*, 1922, **15**, 185—338).—The sorption isotherms for water, alcohol, and acetic acid vapours have been determined at 20°, 25°, 30°, and 35° with animal charcoal as adsorbent. These show that sorption is not a single process. The isotherms, which over the first portion are straight lines (water) or concave to the pressure axis (alcohol and acetic acid), show a well-defined inflexion at the point *O*. At this point the curve rises steeply and becomes convex to the pressure axis (water), or turns, and forms a wedge-shaped peak pointed outwards with respect to the pressure axis (alcohol and acetic acid). In the experiments, the vapours were added to the charcoal in small portions and the sorption equilibria were reached in all cases from both sides. The first part of the curves before the point *O* is reached represents a reversible process, since the points obtained by both methods lie on the same curve, whilst the equilibria points above the point *O* lie on parallel curves. Equilibrium is set up much more rapidly from below than from above. The experimental results are explained in much the same way as the sorption by gels. The sorption occurs first through adsorption and then from the point *O* mainly through condensation of liquid in the pores of the charcoal. The hysteresis observed is explained by the varying curvature of the meniscus during sorption and desorption. This depends on the fact that during sorption the walls of the charcoal pores are only slowly wetted, which in its turn is probably due to the presence of air. When the equilibrium is established from the under side, desorption, a rapid evaporation of the vapour from the charcoal, occurs, whereby the meniscus in the capillaries take on a greater curvature than previously and the equilibrium is rapidly stable. Sorption takes place slowly, because the radius of curvature of the meniscus decreases uninterruptedly while the walls are moist. Thereby a fresh condensation of vapour takes place and the establishment of equilibrium is delayed. The taking up of each portion of vapour added occurs at first by means of adsorption, and the adsorption equilibrium is established in about thirty seconds. Only in the case of charcoal which had been exhausted immediately before the experiment could the adsorption equilibrium be recognised. For this process the formula $k=1/tp_\infty.[\log p/(p-p_\infty)-\log p_0/(p_0-p_\infty)]$ is representative. The structure of charcoal has been discussed, and the radii of the capillaries have been calculated by means of the Trouton and Andersson formula. The taking up of alcohol and acetic acid vapour at 20° occurs in such a way that only capillaries of the same diameter are active. Approximately 75% of the total quantity is taken up at very low pressures, that is by capillaries of very small radius of the order $r<6\cdot2\times10^{-8}$ cm., which indicates that charcoal is possessed of an exceedingly fine structure. The

course of the taking up of water differs from that of the two other liquids inasmuch as the calculated radii are partly much greater and that the maximum volume is smaller. These two circumstances are explained by the smaller power of water to wet the charcoal and by the slow penetration of liquid into the pores of the charcoal. The surface of the charcoal has been approximated from the experimentally determined volume of the empty space of the charcoal and the calculated radii of the capillaries in which condensation occurs. The free surface of the capillaries of radius $r > 6 \times 10^{-8}$ cm. is about 600 sq. metres per gram of charcoal and the total area of all capillary walls $>3000$ sq. metres. Trouton's sorption rule is shown to be incorrect and in its place it is shown that the volume taken up, and not the mass, of a given liquid is independent of the temperature and only a function of the pressure.

J. F. S.

**More General Theory of the Adsorption of Solutions.** Wolfgang Ostwald and Ramon de Izaguirre (*Kolloid Z.*, 1922, **30**, 279—306).—A theoretical paper in which a large number of types of adsorption curves and formulæ have been collected and criticised. The view is expressed that every adsorption is at first a process of "unmixing," whereby a most concentrated solution, the absorbed solution, forms on the surface of the adsorbent whilst the equilibrium solution remains behind. Solutions of substances are adsorbed and not the "dry" dissolved substances. In opposition to the previously held views, the author postulates that the adsorption of the solvent, along with the dissolved substance, is an integral and equally important process in every adsorption from solutions. The assumption is made that the adsorption of the dissolved substances, without reference to the simultaneously adsorbed solvent, increases asymptotically up to the highest concentration in accordance with Boedecker's logarithmic formula. It is shown that this formula is not in keeping with the difference in concentration before and after adsorption, except in the case of very dilute solutions. Since the actual amount of adsorbed substance continuously increases, the difference in concentration $(c_0-c)$ must show a maximum and at the highest concentrations approach the zero value. It is shown that the whole of the adsorption curves may be constructed on the basis of the three assumptions made above and the simultaneous adsorption of the solvent. A number of formulæ are developed which give a quantitative relationship between adsorption and concentration on the basis of the above assumptions. The most important of these are: (1) $N/m(c_0-c)=kc^n(100-c)$ for the case where the adsorption of the solvent may be neglected; (2) $N/m(c_0-c)=kc^n(100-c)-l(100-c)^a.c$ for cases where the solvent is adsorbed directly by the adsorbent; (3) $N/m(c_0-c)=kc^n\{100-c(1+s(100-c)^\beta)\}$ for cases in which the solvent of the adsorbed solution is brought into the surface layer by the solvation of the dissolved substance; (4) $N/m(c_0-c)=kc^n[100-c(1+s(100-c)^\beta)]-l(100-c)^a.c$ for cases in which the adsorption of the solvent takes place by both methods

provided for in equations 2 and 3. In these equations $N$ is the weight of solution in grams at the commencement, $m$ the weight of adsorbent, $c_0$ the initial percentage composition of the solution, $c$ the equilibrium percentage concentration of the solution, $k$, $l$, $s$, $n$, $\alpha$, $\beta$ are constants. A graphic method for evaluation of the constants is described. The second equation has been tested by means of the measurements of Schmidt-Walter for the adsorption of acetic acid and water by charcoal (A., 1914, ii, 542) and Gustafson's measurements of the adsorption of phenol and alcohol by charcoal (A., 1915, ii, 824) and a remarkably good agreement between the calculated and experimental values found.

J. F. S.

**Relationship of Dolezalek's Theory of Solutions to that of Planck.** H. CASSEL (*Z. physikal. Chem.*, 1922, **101**, 235—237).—In earlier papers, Wagner (A., 1920, ii, 596) has shown that Dolezalek's theory of solutions is a special case of Planck's theory of concentrated liquid mixtures, which is of no special importance. The present author shows mathematically that Wagner's conclusions are based on an error. J. F. S.

**Solubility. IV. Principle of the Specific Interaction of Ions.** J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1922, **44**, 877—898; cf. A., 1920, ii, 536; this vol., ii, 199).—It is shown that the activity coefficient of an ion may be determined by two factors, one of which is due to the salting-out effect of the salt solution serving as solvent and the other to electrical interaction between this ion and the ions of the solvent. Ions are uniformly influenced by ions of their own sign; their activity coefficients depend, therefore, only on the action of ions of the opposite sign and the salting-out effect of the solvent. The salting-out effect of a salt solution can be represented as a product of the salting-out effects of the separate ions. A number of relationships are derived for the solubility of salts at constant concentration of solvent solution and methods for determining the ratios of salting-out coefficients, coefficients of interaction, and activity coefficients. Thermodynamic relationships between activity coefficients and osmotic coefficients in solutions of constant total concentration and a relationship between solubility and freezing point are derived. The above theoretical conclusions and relationships are experimentally verified by solubility determinations in solutions of highly complex salts. A method of determining liquid junction potentials, on the basis of the present considerations, is put forward. In the case $0{\cdot}1M KNO_3|0{\cdot}1M NaNO_3$, a small concentration of silver nitrate is added and the *E.M.F.* of the cell $Ag|KNO_3(0{\cdot}1M)AgNO_3(0{\cdot}001M)||AgNO_3(0{\cdot}001M)NaNO_3(0{\cdot}1M)|Ag$ measured. The *E.M.F.* is given by $\pi_1 = RT \log_e fAg(NaNO_3)/fAg(HNO_2) + \pi_d$, where $\pi_d$ is the junction potential and $f$ is the activity coefficient of the Ag in the solution named. Also $\pi_1 = RT \log_e r_{(Na/K)} + \pi_d$ where $r_{(Na/K)}$ is the ratio of the salting-out coefficients of the sodium and potassium ions. This ratio can be determined from solubility measurements and consequently $\pi_d$ may be calculated. J. F. S.

**Hydration of Electrolytes.** S. ASCHKENASI (*Z. Elektrochem.*, 1922, **28**, 106—110).—A theoretical paper in which the deviations of osmotic quantities of moderately and very dilute solutions have been collected together with the inflexion points of the experimental series. The Born-Fajans's polarisation–hydration hypothesis is discussed, and it is shown that the forces assumed in this hypothesis would produce a greater effect on the vapour pressure than is observed experimentally. In Fajans's method of calculating the heat of hydration, the influence of the dielectric constant on the work of dissociation is not taken into account. The author presents a chemical mechanism for hydration in salt solutions on the assumption that the associated liquid molecules of water are modified in the process. On the basis of this view, the author attempts to overcome the objections which have been offered to a step-wise hydration. J. F. S.

**Calculation of the Osmotic and Activity Functions in Solutions of Uni-univalent Salts.** J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1922, **44**, 938—948).—A theoretical paper in which from the point of view that the individualities of salt solutions have an origin similar to that of the individual salting out effect in the case of non-electrolytes, equations are deduced to govern the osmotic and activity functions of uni-univalent salts in pure and mixed solutions. These equations have been tested by means of the most accurate experimental results, which include measurements of depression of the freezing point, solubility, and electromotive force. Ratios of activity coefficients have been calculated on the basis of these equations in conjunction with the principle of the specific interaction of ions. J. F. S.

**The Mutual Solubility of Liquids at High Pressures.** JEAN TIMMERMANS (*Arch. Néerland*, 1922, [iii], **6**, 147—151).—This work completes the previous researches of Kohnstamm and Timmermans (A., 1913, ii, 481). The apparatus employed is described in the previous communication.

*A*.—System water–*sec.*-butyl alcohol. The curve obtained for this system under high pressures is analogous to that of methyl ethyl ketone. With increasing pressure, the lower critical solution temperature (normally below the freezing point, $-8·45°$) is raised and the higher critical temperature, 113·8°, is lowered. Under a pressure of 830 kilos. they meet at about 65°, so that at these high pressures the liquids are miscible in all proportions. The values of $dt/dp$ for both critical values are given. As demanded by theory, $dt/dp$ for the freezing point of water was found to be less than for alcoholic solutions. The alcohol employed had a boiling point 99·50°$\pm$0·01. $d_4^{\circ}$=0·82263$\pm$0·00002.

*B*.—System water–*iso*butyric acid (b. p. 154·35°, f. p. $-47·0°$, $d_4^{\circ}$=0·96819). The three-phase system crystallises at $-3·0°$ at ordinary pressures. The critical solution temperature decreases more rapidly than the temperature of crystallisation as the pressure is increased so that the three-phase region soon disappears below the curve of solidification. By extrapolation, this was found to occur

at −8·2° under a pressure of 625 kilos. *dt/dp* was found to have a fairly constant value of 0·054.

*C.*—System water–phenol. *dt/dp* was found to be very small, but increases with the pressure 0·0036 to 0·0055.

*D.*—System *cyclo*hexane–methyl alcohol. *dt/dp* has a fairly large value, but decreases with increasing pressure 0·0314 to 0·0191.

W. T.

**A New Method of using *X*-Rays in Crystal Analysis.** GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1922, **8**, 90—96).—Certain alterations in the procedure of *X*-ray analysis is described. *X*-Rays belonging to the continuous spectrum are used instead of the line spectrum usually employed. For this purpose, the ordinary *X*-ray tube with a tungsten target is very convenient. The method has the advantage of flexibility, for short penetrating *X*-rays may be utilised, and with these it is possible to investigate crystals of high absorbing power. The method is suitable for both powders and large crystals. The values obtained for the distances between the planes of atoms are independent of the constants of any other crystal. The new methods of measurement are applied to the crystal structure of potassium iodide. One of the "peaks" obtained corresponds with the characteristic line spectrum of iodine.

W. E. G.

**Isomorphism and Ionic Structure.** HANS GEORG GRIMM (*Z. Elektrochem.*, 1922, **28**, 75—81).—A theoretical paper in which author discusses the connexion between ionic structure and isomorphism. It is shown that ions built on the argon type differ considerably in size from those built on the neon type, whilst those of the krypton type are only little larger than those of the argon structure, and those built on the xenon type differ from those of the krypton type by intermediate amounts. Thus the expression $r_A - r_{Ne} > r_X - r_{Kr} > r_{Kr} - r_A$ represents the differences of the ionic radii. The characteristic gradation, of the lattice distances of similarly constructed compounds, in which the variable ions have the same number of exterior electrons, is conditioned by the gradation of the atomic radii. This is shown by the fact that the lattice distances of binary compounds is approximately given by the linear equation $r = \alpha a + \beta k$, in which $a$ and $k$ are the radii of the anion and kation respectively and $\alpha$ and $\beta$ numerical constants. The relationship between isomorphism and ionic structure is shown by means of a table. It is shown that miscibility between ions with the neon and helium structure is unknown, although aluminium hydroxide and boric acid show a slight tendency. In the case of ions of the neon and argon structure, no crystallochemical relationship exists between $O''$ and $S''$, but $F'$,$Cl'$, $Na^{\cdot}$ and $K^{\cdot}$ exhibit miscibility in the case of large molecules and at high temperature, that is, under conditions where the influence of the difference in the radii is overcome. Complete miscibility is found between the ions of the argon and krypton type on account of the small difference between the atomic radii. Ions of the

*krypton and xenon configuration also show close crystallo-chemical* relationships, but the somewhat greater difference between the radii is expressed in the limited miscibility of potassium bromide and iodide. The ions of the argon and xenon structures form the end members of the well-known isomorphous series, but here also *the difference in the ionic radii is shown in the existence of a large* gap in the mixture series of potassium chloride and iodide. In general, the isomorphic relationships are determined by the characteristic gradation of the ionic radii in the case of similarly constituted ions. J. F. S.

**Fundamental Principles of Colloidal Chemistry. I. Electrical Charge of the Particles and New Conceptions of Micellæ.** RICHARD ZSIGMONDY (*Z. physikal. Chem.*, 1922, **101**, 292—322; cf. this vol., ii, 129).—A theoretical paper in which it is shown that the conception expressed by the term micella has been entirely adopted in the various branches of colloidal chemistry. After considering a number of widely differing colloidal systems it is shown that the term micella has been applied to a series of different structures, which the author proceeds to characterise more exactly. Whilst the micellæ of Nägeli are crystalline individual particles, the term is employed by others for particles of very different constitution. It is pointed out that in most modern colloidal research the electrical charge has become the important factor, whilst the study of the particles themselves has been neglected. It is known that colloidal particles can be either crystalline primary particles (colloidal gold, vanadium pentoxide), secondary particles partly filled with liquid (stannic acid, purple of Cassius), or aggregates of molecules and ions of little stability combined with condensation nuclei (soap solutions). Both the primary particles and the secondary particles, depending on the electric charge can exhibit a considerable stability, and then they behave as multivalent ions of substances of very large molecular weight. J. F. S.

**Energy Principle of the Coagulation of Colloids, particularly of the Thermo-kinetic Mechanism.** ROBERT FRICKE (*Z. physikal. Chem.*, 1922, **101**, 185—192).—A theoretical paper in which the heat change of some ideal coagulation processes of hydrosols and gas-dispersoids has been calculated on the basis of the thermo-kinetic shadow theory (A., 1920, ii, 740; 1921, ii, 387). The small heat changes obtained were compared with those calculated from the osmotic work and the work of lattice separation. All values are found to be of small dimensions. A short discussion of the different interdependent heat effects accompanying coagulation is entered on, and it is shown that the electrostatic discharge work must furnish a large portion of the heat of coagulation. The coagulation of discharged colloids in the case of hydrosols is mainly brought about by intermolecular forces (lattice forces) in the sense applied by Zsigmondy, and to a lesser degree by thermokinetic shadow action. In the case of gas-disperse systems the latter assumes an importance which may not be neglected in concerning the actual precipitation. J. F. S.

**Physico-chemical Investigation of Colloidal Sulphur.** G. ROSSI (*Kolloid Z.*, 1922, **30**, 228—230).—In a previous communication (A., 1912, ii, 1037) it was shown that the electrical conductivity of a solution of colloidal sulphur containing sulphuric acid and sodium sulphate is lower than that of a similar solution containing no colloidal sulphur. It is now shown that the freezing point of a solution of the same kind as the above is lower after the colloidal sulphur has been removed than when the colloid is present. Further, if a colloidal sulphur solution containing sulphuric acid and sodium sulphate is dialysed to remove the electrolytes and the same amount of electrolytes added to the dialysed solution, then the electrical conductivity has the same higher value of the solution from which the colloid has heen removed. It is thus shown that the action of the colloidal sulphur extends to sulphuric acid and sodium sulphate even when these are present in quantities larger than those required to stabilise the sol, provided that the excess of these substances was present when the colloid was formed. Further quantities of these substances added after the formation of the colloid are not affected by the colloid. It is therefore assumed that crystalloids, in the form of sulphuric acid and sodium sulphate, undergo a change in their physical nature in the presence of colloids, which is shown by a reduction in the electrical conductivity and the osomotic pressure. J. F. S.

**Cell for the Observation of Colloidal Solutions for Use with Substage Ultra-Condensers.** FRED FAIRBROTHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1071—1072).—A cell is described for use in quantitative work on colloids with substage ultra-condensers. The apparatus eliminates the necessity of readjusting the optical arrangement every time a fresh portion of the colloidal solution has to be examined, as is the case with Burton's method of using a hemacytometer slide ("Physical Properties of Colloidal Solutions," 1921, p. 124). The apparatus consists principally of a circular brass block which has a circular hole in the centre and is bored at two diametrically opposite points to receive two copper tubes 2 mm. diameter. The holes are made so that they pass from the edge of the brass ring to the base. The bottom of the block, which is ground perfectly flat, is carefully cemented to a cover-glass and two holes are bored through the latter to meet the two holes in the base. The arrangement has the advantage of a reinforced cover-glass, and as both surfaces of cover-glass and slide are flat it is not necessary to cement the two together. The apparatus is held in position on the slide while being fixed in position by plasticine. To the copper tubes are fixed a delivery funnel and clip and an exit tube. J. F. S.

**Protective Colloids. XII. Gelatin as a Protective Colloid. Colloidal Silver.** A. GUTBIER, J. HUBER, and A. ZWEIGLE (*Kolloid Z.*, 1922, **30**, 306—313; cf. A., 1921, ii, 312).—The effect of chloroform, toluene, acetone–chloroform, and ethyl acetate in small quantities on solutions of gelatin has been investigated and it is shown that all four substances act as excellent preservatives

for gelatin solutions. In the case of chloroform (10 c.c. per litre c solution), the solutions are stable, and only after weeks does small quantity of a white precipitate separate; with toluene, slight turbidity appears in a 5% gelatin solution after two week but with more dilute solutions no turbidity is observed. Th addition of 1% acetone–chloroform increases the stability of gelati solutions, whilst with 0·5% of ethyl acetate a turbidity appears i two days; this turbidity speedily redissolves and the solution the remains unchanged for forty-two days. The efficiency of gelati as a protective colloid for colloidal silver has been investigated, an it is shown that colloidal silver obtained by reduction with hydrazin may be protected with a small concentration of gelatin and th stability increased, but an excess of gelatin exerts a disturbin influence on the stability. The most stable and at the same tim the most concentrated silver sol is prepared by reducing 10 part of 0·1*N*-silver nitrate in 30 parts of 0·42% gelatin with hydrazin and immediately dialysing for six hours. This sol is reddish brown by transmitted light and olive by reflected light; afte dialysing for ten days a preparation was obtained which containe 40·45% of silver and was stable for three-quarters of a year. Whe the colloidal silver was produced by means of sodium hyposulphit sols were obtained which were much less stable than those reduce by hydrazine. The effect of electrolytes on protected silver so was investigated and it is shown that chlorides (hydrogen, sodiun magnesium, and barium) effect a rapid precipitation of the colloid *N*-sulphuric acid produces a precipitation which is not complet in five days, sodium thiosulphate brings about a slow sedimentatio whilst sodium hydroxide and sodium carbonate in *N*-solutions ai without coagulating action. J. F. S.

**Dependence of the Base Equilibrium in Permutite on th Concentration of the Surrounding Solution.** A. GÜNTHE SCHULZE (*Z. Elektrochem.*, 1922, **28**, 85—89).—The author ha investigated the equilibrium in solutions of two salts of varyi concentrations when shaken with permutite containing the sam kations as the solution, with the object of ascertaining the co centration of the solution which is in equilibrium with the pe mutite. The experiments were carried out at 22° with 50% silve and 50% ammonium, 33·33% copper and 66·67% ammonium, an 4% lanthanum and 96% ammonium permutites, and the solutio contained the respective salts as nitrates. The results show that i a certain measure the demands of the law of mass action are fulfille but until the ionic concentration can be definitely determined cannot be proved that the equilibrium is always set up in keepin with this law. J. F. S.

**The System *iso*Butyl Alcohol–Water.** A. MICHELS (*Arc a Néerland*, 1922, [iii], **6**, 127—146).—The *iso*butyl alcohol was speciall purified, b. p. = 107·47°, $d_4^{\circ}$=0·8197. The higher critical solutio temperature was found to be 132·8° and the pressure 332·5 cm mercury, the critical concentration being 37% alcohol. Crysta

lisation of the mixture prevented the realisation of the lower critical temperature. $dt/dp$ for the critical temperature was found to be less than 0·01. The solubility of the alcohol in water was found to have a minimum value at 58° with a composition corresponding with 7% alcohol. The influence of impurities on the temperature of separation into two layers was very marked; 1% of ethyl alcohol lowered it by 50°, other impurities raised the temperature. Measurements were also carried out of the vapour pressure of the system; these are given in tables for $t-x$ and $p-x$; the latter shows a maximum but the composition corresponding with it could not be definitely fixed; it lies in the three-phase region. Further experiments are being carried out. W. T.

**Influence of the Time Factor on the Interpenetration of Solids by Chemical Reaction.** H. Weiss and P. Henry (*Compt. rend.*, 1922, **174**, 1421—1423; cf. this vol., ii, 207).—The time necessary for a given increase in the zone of interpenetration may be divided into two parts, namely, that required for the chemical reaction once the molecules of the two metals, in this case silver and antimony or copper and antimony, are in contact, and the time necessary for the molecules to traverse the layer already formed. The experiments tend to show that the duration of the chemical reaction is negligible as compared with the time required for the molecules to traverse the layer formed. The experimental points at each temperature fall on two distinct curves which are closely connected with the intensity of the blows of the hammer used to establish contact between the two metals.

W. G.

**The Rate of Evolution of Carbon Dioxide from Solution in Presence of Colloids.** Alexander Findlay and Owen Rhys Howell (T., 1921, **121**, 1046—1052).

**The Influence of Solvents on the Velocity of Formation of Quaternary Ammonium Salts.** James Alexander Hawkins (T., 1922, **121**, 1170—1176).

**The Velocity of Absorption of Carbon Dioxide by Alkaline Solutions.** Paul Riou (*Compt. rend.*, 1922, **174**, 1463—1466).—Velocity curves have been plotted for the absorption of carbon dioxide by solutions of potassium carbonate under different conditions of concentration and temperature and with or without the presence of potassium hydrogen carbonate or potassium chloride. With potassium carbonate alone the velocity of absorption at first increases with the concentration very rapidly to a maximum and then slowly diminishes. The presence of potassium hydrogen carbonate causes a very marked diminution in the velocity of absorption, but the effect of potassium chloride is less marked. In every case, rise in temperature is accompanied by an increase in the velocity of absorption. Other factors being equal, the velocity of absorption is practically proportional to the concentration of the carbon dioxide in the air mixture. W. G.

**Acceleration of the Solubility of Metals in Acids by Reducible Compounds.** H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1449—1454).—The velocity of solution of a metal in an acid is enhanced by the presence of a reducible substance (cf. A., 1918, ii, 13). Nitrobenzene and benzaldehyde accelerate the rate of solution of iron, zinc, lead, tin, copper, nickel, aluminium, and silver in a large number of acids. In the presence of nitrobenzene, the rate of solution is increased up to 1000 times. The increase in the attack on the metal is accompanied frequently by an increased evolution of hydrogen. Benzaldehyde is selective in its action. Benzophenone retards the rate of solution of the metal and the rate of generation of hydrogen from zinc and an acid. Co-action has been realised in a system of four components—a metal, a salt of hydrochloric acid, a feeble acid (acetic acid), and nitrobenzene. W. E. G.

**Landolt's Reaction.** ANTON SKRABAL (*Z. Elektrochem.*, 1922, **28**, 224—244).—The Landolt reaction which takes place in solutions of sulphurous acid and excess of iodic acid has been investigated. This reaction takes place according to the equations (1) $IO_3'+3SO_3''=I'+3SO_4''$, (2) $IO_3'+6H^{\cdot}+5I'=3I_2+3H_2O$, (3) $3I_2+3SO_3''+3H_2O=6I'+6H^{\cdot}+3SO_4$. Of the three partial reactions, 1 and 2 take place slowly with respect to 3 and determine the time of the reaction. Because the rapid reaction 3 follows the slow reaction 2 the sum of the equations of these reactions give equation 1 and consequently until the change of colour occurs equation 1 represents the total reaction. If reaction 2 is made more rapid than 1 by adding iodide to the mixture, then the whole of the sulphite will be oxidised according to 2 and 3 and reaction 2 alone will determine the time of the reaction. According to the measurements of Dushman (A., 1921, ii, 315), the expression $-d[IO_3']/dt=K_2[IO_3'][I']^2[H^{\cdot}]^2$ represents this reaction. At the point of change, the whole of the sulphite has been oxidised, and therefore the initial concentration of this substance is a measure of the time required by reaction 2 to occur. If all the variable concentrations are chosen large with respect to the sulphite concentration, then reaction 2 takes place with constant velocity and the time of the reaction must be proportional to $[SO_3'']/[IO_3'].[I']^2.[H^{\cdot}]^2$. This simple relationship has been experimentally verified. In this form, the Landolt reaction is particularly suited as a lecture experiment for demonstration of reaction velocity. The time law $-d[IO_3']/dt=K_1[IO_3'].[SO_3''].[H^{\cdot}]$ is deduced for both reactions 1 and 2 individually. The constants $K_1$ and $K_2$ have been evaluated and tested over a wide range of concentration and shown to be in keeping with Dushman's experimental results (*loc. cit.*). In connexion with the foregoing experimental investigation, chemical kinetics are discussed generally. It is shown that chemical reactions only follow a definite time law over a limited range of concentrations and velocities. They are subject to a change of time law, so the constant $K_2$ of the iodate–iodide reaction becomes markedly smaller with increasing velocity, as is shown by

ıe present experiments and those of Dushman. The temperature uotients, $Q_{10}=K_{t+10}:K_t$, holds only for a definite total reaction. n the case of the total reactions, $IO_3'+6H^{\cdot}+8I'=3I_3'+H_2O$ and $IO_3'+6HSO_4+8I'=3I_3'+6SO_4''+3H_2O$, the value $Q_{10}$ ; 1·3 for the first and 0·85 for the second. These two temperature uotients are connected through the time law of the total reaction ·ith the heat change of reaction $H^{\cdot}+SO_4''=HSO_4'$. Both total ɜactions have their own heat changes, and the relationship between his and $Q_{10}$ rules the adiabatic course of the reaction. J. F. S.

**Kinetics of Reactions in which Halogen Atoms pass from he Inner Sphere of Activity to the Outer.** H. FREUNDLICH nd R. BARTELS (*Z. physikal. Chem.*, 1922, **101**, 177—184).—The elocity of reaction of the following reactions has been determined uantitatively in some cases and semi-quantitatively in others at ° and 25°. (1) $[Cr(NH_3)_5Br]^{\cdot\cdot}+H_2O=[Cr(NH_3)_5H_2O]^{\cdot\cdot\cdot}+Br'$; (2) $[Cr(NH_3)_5I]^{\cdot\cdot}+H_2O=[Cr(NH_3)_5H_2O]^{\cdot\cdot\cdot}+I'$;

3) $CH_2Br\cdot[CH_2]_3\cdot CH_2\cdot NH_2=CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NH_2^{\cdot}+Br'$; and

4) $CH_2I\cdot[CH_2]_3\cdot CH_2\cdot NH_2=CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NH_2^{\cdot}+I'$. The velocity has been compared with the reactions previously studied A., 1914, ii, 448). The whole of the reactions are shown to conorm with an equation of the first order. The velocity constants ıre dependent on the nature of the halogen and also on the nuclear ıtom; they increase very strongly, up to 100 times, in the order Cl<Br<I, and in the chlorine series they increase 50 times in the order Co<Cr<C. As far as the temperature coefficients were letermined, they were found to be large; the constant $A$ of the Arrhenius equation was about 10,000. This corresponds with the ·ule propounded by Halban, that apparent as well as true unimolecular reactions are characterised by their marked dependence on temperature. J. F. S.

**Course of Simultaneous Reactions.** RUDOLF WEGSCHEIDER Z. *Elektrochem.*, 1922, **28**, 99—100).—In connexion with the statement of Martin and Fuchs (*ibid.*, 1921, **27**, 155) that in the chlorination of methane the concentration of methane and its chlorinated product are dependent on the concentration of one of these substances and quite independent of the time and the chlorine concentration, it is shown that this is not a special case, but is generally true for simultaneous reactions, which with regard to one of the reacting substances, $H$, are of the same order ($n^{th}$). If the reaction equation for two such actions are: $A_1+nH \rightleftharpoons B_1$ and $A_2+nH \rightleftharpoons B_2$ where $A$ and $B$ are complex molecules which do not contain $H$, the equilibrium constants are $K_1=[B_1]/[A_1][H]^n=k_1/k'_1$ and $K_2=[B_2]/[A_2][H]^n=k_2/k'_2$. On subtracting the second equation from the first, the equation $A_1+B_2 \rightleftharpoons A_2+B_1$ is obtained which must represent a possible equation of reaction. If the equilibrium constant of this is $K$, then $K=K_1/K_2=k_1.k'_2/k_2.k'_1=n_{12}/n_{12}'$, where $n_{12}$ is the relationship between the equilibrium constants of the two reactions in the direction left to right and

*$n_{12}'$ in the opposite direction. This shows that the concentrations of all molecular types of A and B at equilibrium are determined by* equations which do not contain the absolute values of the velocities.

J. F. S.

**Mode of Action of Platinum in Oxygen–Hydrogen Catalysis and the Application of Titanium Sulphuric Acid for the Control of the Course of the Change.** K. A. HOFMANN (*Ber.*, 1922, **55**, [*B*], 1265—1274; cf. A., 1920, ii, 240; this vol., ii, 276).—Sensible quantities of hydrogen peroxide are only produced in the surrounding acid during the catalysis of dissolved molecular oxygen and activated hydrogen at platinum surfaces when the reducing power of the hydrogen–platinum electrode is abnormally reduced, when the liquid surrounding the pole contains large amounts of dissolved oxygen, and when the pole is as free as possible from oxides of platinum. It is highly probable that the hydrogen–oxygen catalysis proceeds normally in two stages (1) $O_2+2H=H_2O_2$ and (2) $H_2O_2+2H=2H_2O$. The velocity of the second action at an active platinum surface is, however, so great that hydrogen peroxide does not escape into the surrounding liquid. A specific reducing action towards a third substance of hydrogen peroxide which is liberated at the best only in minute traces is not to be expected in any circumstances. Further, the reduction potential of hydrogen peroxide is much less than the potential of hydrogen activated at a platinum surface.

In preparative or other work in which reductions are to be effected with activated hydrogen, the author recommends the use of the acid titanium sulphate solution for indicating the conditions favourable to maximum reduction or for controlling the course of the change, since the activity of the system is readily shown by the formation of the characteristic violet-brown solutions of tervalent titanium sulphate. In addition, it is to be expected that the reduced titanium will both accelerate and regulate the reducing action since reduced titanium solutions have been successfully utilised on many previous occasions as reducing agents. H. W.

**A Graphical Study of the Stability Relations of Atom Nuclei.** WILLIAM D. HARKINS and S. L. MADORSKY (*Physical Rev.*, 1922, **19**, 135—156; cf. A., 1921, ii, 445, 582, 690).—The following properties are considered graphically: $P$, the number of positive electrons in the nucleus, which is taken to be numerically equal to the atomic weight; $M$, the net positive charge, which is equal to the atomic number; $N$, the number of negative electrons, which is equal to $(P-M)$; $[(N/P)-0{\cdot}5]$, the excess of the relative negativeness $N/P$ over the minimum $0{\cdot}5$; $n$, the isotopic number, which is equal to $(P-2M)$ and also to $(N-M)$. Except in the case of hydrogen and of the helium isotope $P=3$, $N/P$ is never less than 0·5, and $M/P$ is never greater than 0·5. For 85% of the atoms composing the earth's crust, both these ratios are 0·5 and $n=0$. As the atomic number increases, the relative negativeness necessary to stability increases above 0·5; that is, as α-particles are added, extra cementing electrons are required to overcome

*the increasing mutual repulsion of the positive units of the nucleus.* An α-ray transformation does not change *n*, but increases *N/P*, *whilst a β-ray change decreases n by two units and also decreases* *N/P*; thus in each group of isotopes, those with larger values of *N/P* exhibit greater β-ray and less α-ray instability. Stability considerations require that the number of isotopes is on the whole smaller for the lighter atoms. Further, the number of isotopes is larger for even than for odd numbered elements, especially where *M* is greater than 29. For most atoms, *M*, *n*, and *P* are either all even or all odd, but *N* is usually even. The curve for the frequency of occurrence of atoms as a function of *n* shows periodic maxima four units apart, whilst as a function of *M* or *N* the periodic maxima are two units apart. It thus becomes possible to predict the existence of the more abundant isotopes of elements of which the mean atomic weights are accurately known.

A. A. E.

**Spectra of *X*-Rays and the Theory of Atomic Structure.** D. COSTER (*Phil. Mag.*, 1922, [vi], **43**, 1070—1107).—The *X*-ray spectra of the heavier elements are arranged in a scheme which involves the existence of one *K*-level, three *L*-levels, five *M*-levels, and seven *N*-levels in the electronic structure of the atom. These levels are associated with the presence of various sub-groups or shells of electrons in the atom. The rules governing the transference of electrons between the various levels are discussed, and further experimental work is adduced in support of these conclusions. New measurements are made of the *L*-series of *X*-ray spectra of the elements from rubidium to barium. Fourteen lines are recorded and the wave-lengths offer strong arguments in support of Bohr's theory (this vol., ii, 363). Diagrams, based on these lines, are given of the various transitions which have been found to occur between any two levels. Niton, xenon, and krypton are chosen as typical elements. The lines which disappear with decreasing atomic number fall out at the places in the periodic table predicted by Bohr. Certain faint lines in the *L*-series which are connected with the *M*-levels cannot be classified. These and other single lines suggest the existence of new levels associated with only one line. They are attributed, in part, to a more complicated excitation of the atom, due to the removal of two electrons at the same time. W. E. G.

**Structure of Atoms and Molecules in the Light of the Dispersion Theory.** JARL A. WASASTJERNA (*Z. physikal. Chem.*, 1922, **101**, 193—217).—A theoretical paper in which it is shown that the atomic volume is the volume of a sphere constructed round the middle point of the nucleus of an atom and on the surface of which the outside electron system is situated. At a collision of two atoms the minimum distance between the nuclei is equal to the sum of the radii of the orbits of the outside electrons of both atoms. An electrolyte molecule can exist in two modifications, of which the one consists of uncharged and the other of charged atoms or atomic groups. When a molecule is present in

the latter form, it may split into ions if it is present in a mediur of sufficiently high dielectric constant. An equilibrium exist between the two modifications, which lies strongly on the on side for weak electrolytes and strongly on the other side for stron electrolytes. Amphoteric electrolytes may exist in three modi fications. Typical strong electrolytes consist almost entirely c polarised molecules. The above makes possible the calculatio of the true ionic refractions, and thereby the Kossel hypothesi of the structure of the atom can be confirmed in some of it important points. From tbe results of the above-named calculation it follows that the outside sheath of the atoms of the alkali metal contains only a single electron, which in salt formation passe over to the acid radicle. In the case of the alkaline-earth metals the outside sheath has two electrons, which in the same way pas over to the acid radicle. The next sheath of electrons of botl the alkali and alkaline-earth atoms is identical with the outsid system of the elements in the preceding horizontal row, whicl in consequence of the increased attractive force was nearer th centre of the nucleus. The structure of the ions undergoes n great change during the formation of polarised molecules, and th electron orbit of the ions can in most respects be regarded a unchanged. The above can be extended, in all probability, t non-polarised molecules and electro-neutral atoms, except in case where double and treble linkings or rings in the sense adopted b Baeyer are present. J. F. S.

**Separation of Isotopes by Thermal and Pressure Diffusion.** Robert S. Mulliken (*J. Amer. Chem. Soc.*, 1922, **44**, 1033—1051).—The theory of the separation of isotopes by thermal diffusion and by centrifuging is discussed. Equations are developed giving the difference in atomic weight obtainable in any operation, similar to the equations for diffusion and evaporation processes obtained in a previous paper (this vol., ii, 295). For thermal diffusion, the difference in atomic weight between portions of an isotopic gas at temperatures $T_1$ and $T_2$ respectively is $\Delta_t M = K \times B \log_e T_1/T_2$ approximately, the atomic weight being greater at the colder end; $B$ is the ordinary separation coefficient, previously defined, and $K$ is an approximate constant for each element, having a value which is probably about 0·25 and depending on the behaviour of the molecule during impacts. The term $KB$ may be named the thermal separation coefficient. The method of thermal diffusion is shown to be much less effective as a means of separating isotopes than ordinary diffusion or evaporation. A somewhat more advantageous modification of the method is described under the name evaporative thermal diffusion. For the centrifuging of a gas, the difference in atomic weight between the central and peripheral regions is $\Delta_f M = P(v^2 - v_0^2)$, where $P$, the centrifugal separation coefficient, is a characteristic constant for each element and $v$ and $v_0$ are the velocities at the peripheral and central regions of the material under treatment. The values of $P$ for several elements have been calculated and the following are recorded for 20°:

lithium, $1.16\times10^{-12}$; boron, $1.85\times10^{-12}$; neon, $7.38\times10^{-12}$; magnesium, $8.97\times10^{-12}$; chlorine, $14.5\times10^{-12}$; nickel, $18.4\times10^{-12}$; zinc, $53\times10^{-12}$; bromine, $20.4\times10^{-12}$, and mercury, $47\times10^{-12}$. For ordinary air, the coefficient would be $62\times10^{-12}$. The value of $P$ is unaffected by the state of combination of the element, even if the compound contains other isotopic elements. Thus the separation is equally great for all compounds of a given element. This is in contrast to the situation with all the other diffusion methods, for which the degree of separation of a given element in one operation is inversely proportional to the molecular weight of the compound. Further, the value of $P$ for any element is independent of the atomic weight, whilst the ordinary separation coefficient $B$ is inversely proportional to the latter. Hence, the theory is on this basis relatively increasingly more favourable to the centrifugal method as the atomic weight increases. $P=(M_2-M_1)^2x_1x_2/2RT$ for a mixture of two isotopes and for a mixture of several isotopes it has the value $\Sigma_a\Sigma_b x_a x_b(M_a-M_b)^2/2RT$. $P$, unlike $B$, is inversely proportional to $T$, but depends on the atomic or molecular weight intervals $(M_a-M_b)$ and the molecular fractions, $x$, in the same way as $B$. Although for the heavy elements the theory predicts, for a peripheral velocity of $10^5$ cm./sec., a separation many times that obtainable in a single diffusion or evaporation, it is shown that compression and condensation of the gas or vapour into the peripheral region make such large separations impracticable if carried out in the ordinary way. The pressure ratio between the two regions is given by $\log_e p/p_0=M\Delta_pM/2RT\,.\,P$, and so increases with atomic and molecular weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fraction being drawn off very gradually at lower pressure from the centre of the apparatus. The process would be in effect precisely analogous to an evaporation in which the separation coefficient was increased from $B$ to $Pv^2$. This method, applicable at the ordinary temperature to hydrogen chloride, bromide, selenide, telluride, and silicide, might be expected, with peripheral velocities up to $10^5$, to yield a separation ten or fifteen times as great in a single operation as would ordinary diffusion or evaporation. The method may be the most rapid method of separating the isotopes of some of the elements of medium atomic weight, but for the lighter or heavier elements the method is less promising. The theory of the separation of isotopes by centrifuging liquids is discussed, and it is shown that the degree of separation for a given apparatus is identical for liquids, gases, and intermediate states of matter. An attempt has been made to test the theory in the case of mercury, but negative results were obtained which are attributable to a slight vibration of the centrifuge. This effect is likely to prove a limiting factor in any attempt to use the method of liquid centrifuging. A statement made in a previous paper in connexion with the diffusion of an isotopic gas through a thin layer of another gas enclosed in the pores of a membrane (*loc. cit.*) is corrected. This method

*is now found to be always less favourable than molecular diffusio[n] instead of more favourable as previously stated. This is due t[o] the effect of the increased mean free path of the heavier molecule which results* from persistence of velocity. This factor was expressl[y] neglected previously. Further, it is shown that mass motion either positive or negative, should have practically no effect o[n] the rate of separation, except indirectly as it may affect bac[k] pressure. J. F. S.

**The Hydrogen Molecule. III.** ALBERT C. CREHORE (*Phil Mag.*, 1922, [vi], **43**, 1025—1038; cf. A., 1921, ii, 632; this vol. ii, 438).—A theoretical investigation into the stability of the author'[s] model of the hydrogen molecule. On this view, the forces betwee[n] the electrons and nuclei cause slight deformations of the shape o[f] the electrons. Two of the electrons in the molecule are flattene[d] and two are expanded in the direction of the minor axis, and thes[e] processes may be accompanied by energy changes which may b[e] either positive or negative in sign. These energy changes, whic[h] are slight compared with the total energy of the electron, corre spond with the heat of dissociation or heat of reaction. Th[e] change in mass which occurs on dissociation is so small that i[t] must escape experimental detection. W. E. G.

**The Abnormally Long Free Paths of Electrons in Argon** J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **43** 1127—1128).—A continuation of an investigation into the mea[n] free path of the electron in various gases (cf. this vol., ii, 277) From experiments on mixtures of hydrogen and argon, it is deduce[d] that the mean free path in argon at 1 mm. pressure is about 15 mm. or fifty times the mean free path calculated from the atomic radiu[s] of argon. W. E. G.

**Some Linear Relationships in the Periodic System.** WILHELM BILTZ (*Z. Elektrochem.*, 1922, **28**, 65—70).—A theoretica[l] paper in which a number of linear relationships between the properties of the elements are described. The relationships describe[d] are in every case between the inactive gases and the other elements In the case of atomic volume, it is shown that this quantity for a halogen is proportional to the value for the inactive gas which precedes it in the periodic system. The expression: at. vol. (halogen)$=a\times$at. vol. (inactive gas)$+b$, where $a$ and $b$ are constants and have in this case the values 0·8015 and zero respectively Taking the atomic volumes of the inactive gases as known, the corresponding values for the halogen are given with an error of $\pm 0{\cdot}2\%$. Similar straight line relationships are found for the atomic volumes of potassium, rubidium, and cæsium; titanium, zirconium, and cerium; and silicon, germanium, and tin; but fo[r] no other cases. In the same way, the boiling points of the halogens are connected with those of the inactive gases by the equatio[n] b. p. (halogen)$=2{\cdot}753\times$b. p. (inactive gas)$-1{\cdot}8$. Here the accurac[y] is the same as before. If hydrogen is included with the halogens, the relationship b. p. (halogen)$=2{\cdot}705\times$b. p. (inactive gas)$+8{\cdot}5$ is

accurate to ±2·5%. In the case of the critical temperature, the expression $T_c$ (halogen)=2·648 $T_c$ (inactive gas)+18·1 is true absolutely both for the halogens or hydrogen. The atomic refraction of the halogens and hydrogen are connected with the similar value of the inactive gases by the expression $R_D$ (halogen)=$R_D$ (inactive gas)+0·41. In this case, the divergence between the calculated and experimental values nowhere exceeds the experimental error. For the elements of the sulphur group $R_D$ (element)=1·713 $R_D$ (inactive gas)+1·15 is true to ±1·8%, whilst for hydrogen and the alkali metals $R_D$ (alkali metal)=1·13 $R_D$ (inactive gas)+0·51 with an error of ±1·5%. The atomic radii of the halogens, elements of the sulphur group, and the alkali metals are connected to within ±1·0% with the corresponding values for the inactive gases by the expressions $r$ (halogen)=0·78 $r$ (inactive gas)+0·26, $r$ (S element)=0·645, $r$ (inactive gas)+0·53, and $r$ (alkali metal)=1·18 $r$ (inactive gas)−0·23. From a consideration of the foregoing, the author deduces periodic constants. J. F. S.

**The Determination of the State of Valency of Lower Compounds by means of Ammoniacal Silver Solutions.** Oscar Olsson Collenberg (*Z. anorg. Chem.*, 1922, **121**, 281—297).—The author has investigated this method of determining valency (introduced by Philipp and Schwehel, *Ber.*, 1897, **12**, 2234) with respect to suitable conditions of experiment and accuracy of results. If the reaction takes place on the water-bath, the best results are obtained with concentrated ammonia and not too great an excess of silver nitrate in a comparatively small volume. The results obtained are low, but suitable for valency determinations, wholly unsuitable, however, for accurate work, such as determination of purity. If the reaction has to be carried out at a high temperature and under pressure, then a large excess of silver salt in concentrated ammonia is necessary; the temperature should be kept as low as possible and not maintained longer than necessary. The best results were obtained by using silver chloride or sulphate, in the presence of cyanides; silver nitrate should not be used. Ammonia generally contains reducing impurities (organic bases) and a blank experiment should be carried out. W. T.

**Observations on the Construction and Use of the Steele-Grant Microbalance.** E. J. Hartung (*Phil. Mag.*, 1922, [vi], **43**, 1056—1064).—A description of the Steele-Grant microbalance used in the study of the action of light on the silver haloids (T., 1922, **121**, 682). A balance with a double knife-edge and giving a sensitivity of 1 in $10^6$ was sufficiently accurate for the proposed work. For this type the simple double triangle type of beam is recommended; a single knife-edge balance constructed in this manner gave a sensitivity of 1 in $10^7$. Details are given of the grinding of the knife-edges and the drawing of the suspension fibres. Damage to the fibre suspension is avoided by the attachment of a double hook to the end of the quartz weights; this facilitates the removal of the objects from the balance. The author discusses the various sources of error in manipulation,

affecting the sensitivity of the balance, and producing apparent changes in weight. W. E. G.

**Extraction of Small Quantities of Liquids by the Soxhlet Apparatus.** HEINRICH HANDORF [*Z. angew. Chem.*, 1922, **35**, 257—258 (D.R.-P., 807757 and 809512)].—A glass vessel is inserted in the Soxhlet apparatus. In cases where the liquid is to be extracted by a solvent lighter tban itself, this vessel has above it a funnel, the stem of which extends to the bottom of the vessel and ends in a rose. The liquid to be extracted is placed in the vessel and is covered by a layer of the solvent. Condensed solvent drops into the funnel, emerges in drops from the rose, and rises through the liquid. In the case of a liquid being extracted by a solvent heavier than itself, a short funnel ending in a capillary rests on the top of the vessel, and a tube opening near the bottom of the vessel passes through its wall at a suitable height. The condensed solvent falls through the liquid and passes through the tube to the outside of the vessel. The apparatus is suited for the extraction of colloidal liquids. Quantitative extraction is attained. H. M.

**Rhythmic Deposition of Precipitated Vapours.** ENOCH KARRER (*J. Amer. Chem. Soc.*, 1922, **44**, 951—954).—When two narrow cylinders containing respectively small quantities of aqueous solutions of ammonia and hydrochloric acid are placed under a large glass container and so placed that there is a lateral temperature gradient in the container, a series of rings of ammonium chloride forms on the inside of the cylinder which contains the hydrochloric acid. The number of rings varies with the conditions from 1 per cm. to a very large number. These rings mark the edges of disks, so that the vapour space above the hydrochloric acid may be regarded as divided into a number of compartments by disks of ammonium chloride. Within the cylinder each compartment marks the boundaries of a system of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient. J. F. S.

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## Inorganic Chemistry.

**Some Properties of Hydrogen Desorbed from Platinum and Palladium.** PAUL ANDERSON (T., 1922, **121**, 1153—1161).

**The Radius of Hydrogen Atoms in Crystals.** G. AMINOFF (*Geol. För. Förh.*, 1921, **43**, 389—396).—It is calculated that the radius of the hydrogen atom in magnesium hydroxide and manganese hydroxide, the elementary parallelepipeds of which are hexagonal, is, respectively, 1·15 and 1·01 Å.U., whilst in ice the radius is 1·12 Å.U. It is shown that the structure $R^{II}(OH)_2$ may be regarded as ice, $H_2OOH_2$, of which one $H_2$ group has been

replaced by a bivalent metal ion, $R^{II}$. This explains why the group $\frac{HO}{OH}$ of ice has practically the same dimensions in these hydroxides. The relatively high value calculated for the radius of the hydrogen atom is considered to be in keeping with the relation of hydrogen to the alkali metals. CHEMICAL ABSTRACTS.

**An Attempt to Separate the Isotopes of Chlorine.** E. B. LUDLAM (*Proc. Camb. Phil. Soc.*, 1922, **21**, 45—51).—(Sir) J. J. Thomson has suggested (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 87) a method of separation of isotopes based on the number of impacts per second of the molecules of a gas on a liquid surface. The number of impacts will be in inverse ratio to the square root of the mass. If on striking the surface the molecules are removed by solution or chemical action, the composition of the residual gas should steadily alter. Hydrochloric acid at a pressure of a few centimetres of mercury was passed over (*a*) a water surface, and (*b*) ammonia gas, and a small fraction allowed to remain uncombined. No change in the molecular weight was observed after either process. The failure to obtain a separation indicates that the determining factor in the recombination of ammonia with hydrochloric acid is not mere collision. W. E. G.

**Fractional Diffusion of Iodine Vapour.** EMIL KOHLWEILER (*Z. physikal. Chem.*, 1922, **101**, 218—234).—Iodine has been subjected to a careful fractional diffusion, and the combining weight of the original material as well as that of the various fractions has been determined by conversion of the iodine into iodide and precipitation as silver iodide. Seventeen determinations with ordinary pure iodine gave a mean value of 126·93, the extreme values being 126·92+0·073% and 126·92−0·079%. Seven determinations with the first fraction of the diffusion gave the value 126·07, which differs by 0·67% from the accepted value for iodine, whilst fourteen determinations with the end fraction gave 127·18, with a divergence of 0·21% from the usual value. These results indicate that, in addition to the isotope of combining weight 127 indicated by Aston, there are at least two others, one lighter and the other heavier than Aston's isotope. It is shown that Aston's results and the present results are not necessarily opposed to one another, for the sensitiveness of Aston's measurement is of the order 5%, whilst that of the present work is much sharper. J. F. S.

**Revision of the Density of Oxygen Gas.** E. MOLES and F. GONZÁLEZ (*Anal. Fís. Quím.*, 1922, **20**, 72—80; cf. A., 1921, ii, 546).—Measurements were made on oxygen prepared in different ways as described in the former paper. The arithmetical mean of forty-five determinations gave the value 1·4892±0·00007 as the weight of a litre of oxygen at 0° and 760 mm. This value is identical with the mean of two hundred and thirteen previous determinations by other workers. The corresponding value calculated for latitude 45° is 1·42897. G. W. R.

**Researches on Sulphuryl Chloride. II. A New Chlorinating Agent: Preparation of Polychloro-derivatives of Benzene.** OSWALD SILBERRAD (T., 1922, **121**, 1015—1022).

**The "Dynamic" Allotropy of Tellurium.** A. DAMIENS (*Compt. rend.*, 1922, **174**, 1344—1346).—Density determinations made on tellurium carefully purified by distillation in hydrogen and then in a vacuum, the material being subsequently crystallised either by vaporisation or by slow cooling of the molten material, do not confirm the views of Cohen and Kröner (A., 1913, ii, 315) as to the dynamic allotropy of tellurium. Tellurium obtained by vaporisation has *d* 6·310, and is not changed by long heating at various temperatures. Specimens prepared in other ways show a slightly lower density, as, owing to the manner of preparation, they are slightly porous. Amorphous tellurium has *d* 5·85—5·87; on heating, it is transformed into crystalline tellurium with development of heat and its density rises. W. G.

**The Reactivity of Ammonia.** EDWARD CHARLES CYRIL BALY and HERBERT MAXWELL DUNCAN (T., 1922, **121**, 1008—1014).

**Polymorphism of Arsenic.** PORPHYRY NICOLAEVITCH LASCHTSCHENKO (T., 1922, **121**, 972—978).

**Flocculation of Colloidal Arsenic Sulphide. Influence of the Concentration of the Colloid, Shaking, and Temperature.** A. BOUTARIC and M. VUILLAUME (*Compt. rend.*, 1922, **174**, 1351—1353).—The influence of different factors varies with the nature of the electrolyte used to cause flocculation. With chlorides of potassium, barium, magnesium, or manganese, the velocity of flocculation increases with the concentration of the colloid, but with aluminium or cadmium chlorides the velocity diminishes as the concentration increases. In comparing once shaking to mix the colloidal solution and the electrolyte, and continuous stirring, the opacity curves for the two conditions superpose one another. With potassium chloride, flocculation of the continuously stirred solution only occurs after the opacity limit has been reached, but with barium or aluminium chlorides flocculation occurs before the opacity limit is reached. The velocity of flocculation varies inversely as the temperature where potassium, sodium, ammonium, or lithium chloride is the electrolyte, directly as the temperature with barium, calcium, strontium, magnesium, or cadmium chloride, and is independent of the temperature with aluminium chloride.
W. G.

**The Isotope Ratio of New Zealand Boron.** ALEXANDER DONALD MONRO (T., 1922, **121**, 986—988).

**The Potassium Salt of Hexahydrodioxydiboron.** RAMES CHANDRA RAY (T., 1922, **121**, 1088—1094).

**The System Potassium Sulphate–Aluminium Sulphate–Water at 25°.** HUBERT THOMAS STANLEY BRITTON (T., 1922, **121**, 982—986).

**Use of Röntgen Rays in Determining the Structure of the ·ystals of Lithium and of some of its Compounds with ght Elements. I.** J. M. Bijvoet and A. Karssen (*Proc. . Akad. Wetensch. Amsterdam*, 1922, **23**, 1365—1370).—The hium atoms in lithium metal are arranged in a centred cubic ttice with a lattice parameter $a=3\cdot50\times10^{-8}$ cm. The relative tensities of the lines are explained by either (*i*) a simple centred bic lattice or (ii) a centred cubic lattice with electrons revolving circles normal to the trigonal axes. There is no evidence for e presence of a lattice of stationary valence electrons. The omic diameter is $3\cdot04\times10^{-8}$, in agreement with the value given y Bragg ($3\cdot00\times10^{-8}$). W. E. G.

**Crystal Structures of Alkali Haloids.** Eugen Posnjak and alph W. G. Wyckoff (*J. Washington Acad. Sci.*, 1922, **12**, 48—251).—Further *X*-ray determinations (this vol., ii, 214) are ven for *lithium chloride, bromide*, and *iodide*, and for *sodium*, otassium, rubidium, and cæsium fluorides. The *X*-ray constants r the whole series of twenty salts RX are tabulated. The strucıres of cæsium chloride, bromide, and iodide are of the bodyentred type, whilst all the others are of the rock-salt type of the mple cubic lattice. L. J. S.

**The Preparation of Ammonium Nitrate.** (Mlle) Wurmser *Compt. rend.*, 1922, **174**, 1466—1468).—Le Chatelier has previously iven a square diagram showing the states of equilibrium between he solution of the four salts ammonium chloride, sodium nitrate, odium chloride, and ammonium nitrate and the solid salts at 16°. similar diagram showing the states of equilibrium at 100° is now iven. The curves at 16° and 100° are essentially of the same hape, and from them it is possible to determine the best experinental conditions for obtaining the maximum yield of ammonium iitrate from a solution of the four salts. W. G.

**The Properties of Ammonium Nitrate. II. Ammonium Nitrate and Water.** Ida L. Millican, Alfred Francis Joseph, and Thomas Martin Lowry (T., 1922, **121**, 959—963).

**The Properties of Ammonium Nitrate. III. Ammonium Nitrate and Sodium Nitrate.** Reginald George Early and Thomas Martin Lowry (T., 1922, **121**, 963—969).

**The Transformation of Ammonium Carbamate.** C. Matignon and M. Fréjacques (*Bull. Soc. chim.*, 1922, [iv], **31**, 394—412).—A résumé of work already published (A., 1920, ii, 250; 1921, ii, 33; this vol., ii, 272). W. G.

**Crystal Structure of Ammonium Fluosilicate.** Richard M. Bozorth (*J. Amer. Chem. Soc.*, 1922, **44**, 1066—1070).—The crystal structure of ammonium fluosilicate has been shown to be like that of ammonium chloroplatinate, ammonium chlorostannate, and potassium chlorostannate, namely, the structure is that of fluorspar in which each fluorine atom is replaced by an ammonium

group, and each calcium atom by a fluosilicate group with the six fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystals (cf. this vol., i, 441). The length of the cube constituting the unit of structure containing four molecules was found to be 8·38 Å.U.; the corresponding lengths for the three complex salts mentioned above being respectively 9·84, 10·05, and 9·96 Å.U. The shortest distance between the centres of the atoms of fluorine and silicon is 1·72 Å.U., whilst the sum of the Bragg radii for these atoms is 1·84 Å.U. The corresponding distances between the platinum or tin and the chlorine atoms in the other three salts are 2·3, 2·46, and 2·44 Å.U., respectively.

J. F. S.

**The Preparation of a Silver Amalgam of the Composition $Hg_3Ag_2$ by Precipitation from a Solution of Silver Nitrate in Pyridine.** ROBERT MÜLLER and REINHOLD HÖNIG (*Z. anorg. Chem.*, 1922, **121**, 344—346).—Metallic needles were formed by keeping a drop of mercury in contact with a solution of silver nitrate and cuprous iodide in anhydrous pyridine. With silver nitrate solution alone, crystals of mercurous nitrate were deposited and a liquid amalgam was formed. The *E.M.F.* of the cell $Ag|0{\cdot}1NAgNO_3$ in pyridine$|Hg$ is 0·038 volt, the silver being negative. For the formation of the metallic crystals, the addition of an approximately equal amount of cuprous iodide is necessary (1 : 1); the addition of a much smaller amount (1 : 10) causes the precipitation of finely divided black silver, too large amounts (5 : 1) change the drop of mercury into a granular powder. The concentration of the silver ion in pyridine is not increased by the addition of cuprous iodide, the concentration cell $Ag|0{\cdot}1NAgNO_3$ in pyr. sat. with $Cu_2I_2|0{\cdot}1NAgNO_3|Ag$ having an *E.M.F.* of 0·37 volt, the silver in the mixed solution being negative. The formation of a blue precipitate of cupric iodide indicates that the silver salt is reduced to metallic silver, whilst the cuprous salt is oxidised to the cupric salt. The cuprous-cupric potential is +0·18 volt, being greater than that of mercury. Cuprous iodide can be replaced by cerous chloride, the separation of crystals being, however, much slower. Ferrous bromide gave a negative result; in water, the ferrous ferric potential is +0·75 volt, but in pyridine it is evidently less than the mercury potential. The amalgam which crystallises in needles corresponds in composition with the formula $Hg_3Ag_2$. The potential of the cell $Hg_3Ag_2|AgNO_3,Cu_2I_2|Ag$ equals 0·37—0·38 volt, the silver being negative against the amalgam.

W. T.

**Attempts at a Synthetic Manufacture of Mother-of-Pearl by Production of Chemical Tracery.** CLÉMENT and RIVIÈRE (*Compt. rend.*, 1922, **174**, 1353—1356).—By precipitating calcium carbonate in the presence of colloidal protein material, such as gelatin in thin layers, a deposit has been obtained having a nacreous structure. The deposit becomes opaque on prolonged drying at 50°, just as mother-of-pearl or pearl itself "dies" when dried for a long period. These experiments support the accepted views as

to the physical and chemical composition of mother-of-pearl and fine pearl. W. G.

**Action of Various Analytical Reagents on Chemical Glassware.** W. E. S. TURNER and T. E. WILSON (*J. Soc. Glass Technology*, 1922, **6**, 17—20).—The tests were made on three types (two English, one French) of chemical glassware; in most cases the solution was kept in contact with the glass for three hours at 100°. Nitric acid (*d* 1·2), and 2*N*-ammonium sulphide solution had but little action on the glasses, but the latter were attacked to an appreciable extent by *N*/2- and *N*/4-sodium phosphate solutions. The French glass was attacked to a greater extent than were the English glasses by the sodium phosphate solutions, whilst there was but little difference between the three types as regards their resistance to alkali hydroxide solutions, showing that the corrosive action of the alkali salt solutions was not due entirely to their alkalinity. W. P. S.

**Solubility of Crystallised Strontium Hydroxide.** D. SIDERSKY (*Bull. Assoc. Chim. Sucr.*, 1921, **39**, 167—177).—Tables and graphs are given showing the solubility of crystallised strontium hydroxide in water at temperatures varying from 0° to 101·2° (b. p. of the solution); at 0°, 100 grams of the solution contain 0·90 gram of $Sr(OH)_2,8H_2O$; at 15°, 1·46 grams, and at 101·2°, 49·75 grams. Other tables give the solubility of the hydroxide in sucrose solutions at different concentrations and temperatures. At 15°, 100 grams of 10% sucrose solution dissolve 3·79 grams of $Sr(OH)_2,8H_2O$, whilst 100 grams of a 25% solution dissolve 7·31 grams of the hydroxide. W. P. S.

**The Reaction of Magnesium Salts with Acid Potassium Pyrantimonate.** MILIVOJ OBAJDIN (*Rad. Acad. Sci. Zagreb*, 1922, **226**, 220—233).—The preparation of *magnesium dihydrogen orthantimonate* by addition of a magnesium salt to a solution of dipotassium dihydrogen pyrantimonate is described; according to the concentration, it is obtained either as hexagonal or monoclinic crystals or in the amorphous form. From a solution containing 1% of the pyrantimonate, both hexagonal and monoclinic crystals and a large quantity of the amorphous precipitate are deposited. From a solution containing 0·35% of the pyrantimonate monoclinic crystals are alone deposited, whilst a solution containing 0·07% of the potassium pyrantimonate yields hexagonal crystals only. The composition of both hexagonal and monoclinic crystals corresponds with the formula $Mg(H_2SbO_4)_2,10H_2O$. The crystals lose 10[?8]$H_2O$ if heated at 176°. When heated further, they lose $2H_2O$ and change their colour successively from colourless to pink orange-yellow, yellowish-green, greyish-green, greyish-blue, and violet, a fact which is probably due to the formation of various polymerides. Finally, the crystals spontaneously incandesce and turn white. The composition corresponds now with magnesium metantimonate, $Mg(SbO_3)_2$. The magnesium dihydrogen orthantimonate, *d* 2·57, is insoluble in alcohol; the solubility in water at 16° is 0·7075 gram in 1000 grams of solution. S. S. M.

**Phosphorescent Zinc Sulphide.** A. A. GUNTZ (*Compt. rend* 1922, **174**, 1356—1358).—The wurtzite and sphalerite forms ( zinc sulphide prepared by heating the precipitated sulphide ar both phosphorescent. They may be distinguished under th microscope by their crystalline structures, but show no differenc in density. Phosphorescence only develops in the presence of trace of a heavy metal. The phosphorescence of wurtzite is mor persistent than that of blende, but in both cases the decrease c luminous intensity is extremely rapid. Under the influence c heat and shock, the two varieties are extremely thermoluminescer and triboluminescent. W. G.

**The Substance between the Crystallites of Metallic Sub stances.** G. TAMMANN (*Z. anorg. Chem.*, 1922, **121**, 275—280).— A piece of metal formed from a regulus consists of crystallite surrounded by a film of impurities which form the residue whe the metal is dissolved in a solvent. To study the structure c these thin layers of impurities it is necessary to employ a trans parent solvent; the evolution of gas and convection current should be avoided, as these destroy the structure. A sheet c cadmium was dissolved in ammonium nitrate, and the film wa found to have a net-like structure, in the meshes of which wer micro-crystals of the metal. When the cadmium was dissolved i hydrochloric acid, the net structure was destroyed by the evolutio of gas and the foreign substance was left as suspended particles The amount of impurity was very much decreased by distilling th cadmium in a vacuum. The author points out the desirability c methods to render these non-metallic impurities visible, to estimat them quantitatively, and to find their influence on the propertie of the metal. W. T.

**Monoclinic Double Selenates of the Cadmium Group** A. E. H. TUTTON (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 245—264).—A in the manganese group (this vol., ii, 505), only three salts, those c rubidium, cæsium, and ammonium, could be obtained in the cadmiur group of hexahydrated double selenates (cf. preceding abstract). Th rubidium and cæsium salts were only obtained with great difficult at a low temperature. No optical investigation was possible o these two salts, and a few optical determinations on the ammoniur salt were only just possible, as the crystals rapidly become opaque The salts crystallise in the holohedral-prismatic class of the monc clinic system.

Rubidium cadmium selenate, $Rb_2Cd(SeO_4)_2,6H_2O$, $a:b:c=$ $0{\cdot}7402:1:0{\cdot}5026$; $\beta=105°\ 7'$. The crystals are metastable dow to 0°. Cæsium cadmium selenate, $Cs_2Cd(SeO_4)_2,6H_2O$, $a:b:c=$ $0{\cdot}7319:1:0{\cdot}5011$; $\beta=106°\ 22'$. This salt is less unstable tha the rubidium salt. Ammonium cadmium selenate, $a:b:c=$ $0{\cdot}7418:1:0{\cdot}5026$; $\beta=106°\ 1'$; $d_4^{20}$ 2·450.

The results of thirty-two years' work on the double sulphate and selenates of the series $R_2M\left(\begin{matrix}S\\Se\end{matrix}O_4\right)_2,6H_2O$ are discussed, in th course of which seventy-five salts, comprising nineteen distinc

roups, have been examined. In each group it is shown that here is a regular progression in the minutest details of the structural and physical properties of the crystals as the atomic number f the alkali metal increases in passing from potassium (19) to ubidium (37) and cæsium (55). The ammonium salt is always ractically isostructural with the rubidium salt of the same group. 'hese results are in agreement with the recently developed theories f atomic and crystalline structure of Langmuir and W. L. Bragg.

E. H. R.

**Tellurium Lead and Tellurium Antimony Alloys.** MAX )REIFUSS (*Z. Elektrochem.*, 1922, **28**, 100—101, 224).—When lead s added in small quantities of molten tellurium, a portion of the ead forms a slag with the tellurium and a small amount of tellurium asses into solution. Tellurium has a deoxidising action on lead, o that lead containing tellurium may be heated to redness without he free liquid surface losing its brightness. Alloys containing ellurium and lead may be prepared by mixing tellurium with nolten antimony; here a continuous series of mixed crystals is ormed. To the molten alloy small quantities of antimony–lead illoy are added and eventually pure lead. A stiff, pasty mass is obtained which on heating at 700° becomes liquid and does not readily lose its bright surface. In the same way, small quantities of tin and copper alloy with the antimony tellurium alloy. The addition of 2% tellurium to lead–antimony alloys has no marked effect on the hardness. The addition of 5—6% of tin to antimony–ead alloys produce much more desirable properties than does ellurium.

J. F. S.

**The Structure of the Isomorphous Group, $Pb(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$.** L. VEGARD (*Z. Physik*, 1922, **9**, 395—410).—The space lattice of this isomorphous group of compounds has been determined by the application of the powder method. Little difficulty was experienced with the nitrates of lead, barium, and strontium, but the deliquescent calcium salt gave less satisfactory results. The positions of the maxima of reflection show that the crystals are not built up entirely of face-centred lattices. The metal atoms are arranged, however, in a face-centred lattice, for the intensity of the maxima of this lattice increases with increasing atomic weight of the metal. Three oxygen atoms and one nitrogen atom form a group at four corners of a cube. This group, which possesses a trigonal axis, is surrounded by four atoms of the metal.

The values for the atomic radii of nitrogen and oxygen atoms are appreciably higher than in those substances investigated by W. L. Bragg. The atomic radii vary with the nature of the chemical combination and the geometrical arrangement in space. The *X*-ray method provides a useful method for the determination of the density of solid substances. The presence of impurities scarcely affects the lattice constants or the atomic radii, from which the density may be calculated. Thus the density of the *pure* substance can be accurately determined from impure material. The values

for the densities of the compounds in the isomorphous group of nitrates, calculated from the atomic radii, are in good agreement with the experimental results. W. E. G.

**Thallic-Thallous Sulphate. I.** A. BENRATH and H. ESPENSCHIED (*Z. anorg. Chem.*, 1922, **121**, 361—362).—Many double salts of thallic and thallous sulphates are claimed by different authors, but the present authors could obtain only two corresponding in composition with $Tl_2SO_4,Tl_2(SO_4)_3$ and $5Tl_2SO_4,Tl_2(SO_4)_3$; all the other so-called double salts are to be regarded as mixtures of these. The preparations and methods of analysis are given. The double salt, $Tl_2SO_4,Tl_2(SO_4)_3$, has a transition temperature of 48° with a fairly large transition interval. The double salt interval for $5Tl_2SO_4,Tl_2(SO_4)_3$ has its upper limit between 23° and 30°. Between this transition temperature and 48° the whole system is in a transition state, so that at these temperatures mixtures of variable composition will be obtained. W. T.

**Determination of the Complex Formation in Aqueous Solutions of Copper Salts by Means of Permutite.** A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1922, **28**, 89—99).—The complex formation in solutions of copper chloride, acetate, formate, sulphate, chlorate, nitrate, and bromide has been investigated by shaking known concentrations of the salts with pure potassium permutite. From measurements of the exchange of kations between the permutite and the solution, conclusions may be drawn as to the presence of complexes in the solution. It is shown, by this method, that the simple complex kation $CuR^{\cdot}$ is present in practically all the copper salt solutions examined even at the greatest dilutions. The presence of the complex $Cu_2R_3^{\cdot}$ has been proved only in the case of copper chloride and bromide, whilst it is probable that the other salts exhibit a higher complex formation, which, however, is not present in such great concentrations. The complexity of copper salt solutions increases at constant concentration with the strength of the acid, and is greater with the salts of halogen acids than with the salts of oxygen acids of equal strength. J. F. S.

**Extraction and Purification of Scandium from Thorveitite from Madagascar.** PIERRE URBAIN and G. URBAIN (*Compt. rend.*, 1922, **174**, 1310—1313).—The finely ground mineral is fused with sodium hydroxide and the product extracted with water. The insoluble residue is dissolved in the least possible quantity of sulphuric acid, and the rare earth metals are precipitated as fluorides by the addition of an excess of hydrofluoric acid. The fluorides are decomposed by sulphuric acid, and scandium hydrogen sulphate crystallises out on concentrating the solution. The sulphates are converted into nitrates by passage through the hydroxides, and the solution of nitrates is evaporated and heated on a water-bath for a long time to free it from excess of acid. To the concentrated solution an excess of powdered potassium sulphate is added until the solution is saturated with this salt. After three days, the double scandium potassium sulphate is collected and washed as

quickly as possible with a saturated solution of potassium sulphate. Any scandium remaining in the mother-liquors is precipitated as hydroxide and put through the same process. The double sulphate may be dissolved in aqueous ammonium carbonate, and from the solution, on warming, scandium hydroxy-carbonate is precipitated. The residue of the scandium in the mother-liquors may be recovered by conversion into its acetylacetonate, which is soluble in chloroform and sublimes when heated in a vacuum at 200°. W. G.

**The Atomic Numbers of Neo-ytterbium, Lutecium, and Celtium.** G. URBAIN (*Compt. rend.*, 1922, **174**, 1349—1351).—An historical paper in which the author points out that Dauvillier's work (this vol., ii, 463) completes the work of Moseley, himself, and others, and definitely establishes celtium as a chemical element with the atomic number 72, and having an atomic weight between that of lutecium, 175, and that of tantalum, 181·5. W. G.

**The Measurements of the Densities of the Haloids of Aluminium with Mercury as Pyknometer Liquid.** WILHELM BILTZ and WALTER WEIN (*Z. anorg. Chem.*, 1922, **121**, 257—265).—The author in previous communications (A., 1921, ii, 437; 1922, ii, 487) has discovered an abnormality in the linear relations in the atomic and molecular volumes of the haloids of aluminium. Former workers (Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii], **58**, 279) used "oil of naphtha" as the pyknometer liquid. Inaccuracies due to the solubility of the bromide and iodide of aluminium in this liquid led the author to replace it by mercury. Toluene was employed in the case of the chloride, on which it has no action. Improved methods of preparation of the haloids are given, and density determinations are described. The densities and molecular volumes were found to be: aluminium fluoride ($d_4^{25}$ 3·10), 27·1; aluminium chloride ($d_2^{25}$ 2·44), 54·7; aluminium bromide ($d_4^{25}$ 3·01), 88·7; aluminium iodide ($d_4^{25}$ 3·98), 102·5. These values, however, do not show the linear relationship exhibited by all other haloids. Other abnormalities are found in the physical constants of the haloids of aluminium, for example, the melting point of the bromide does not lie between those of the iodide and chloride. These are ascribed to polymerisation to double molecules, [$Al_2F_6$], [$Al_2Cl_6$], [$Al_2Br_6$], and [$Al_2I_6$]. These double molecules correspond with cryolite, [$AlF_6$]$Na_3$, the three univalent sodium atoms being replaced by one tervalent aluminium atom thus: [$AlF_6$]Al, [$AlCl_6$]Al, [$AlBr_6$]Al and [$AlI_6$]Al. An *X*-ray examination is necessary to test this explanation. W. T.

**Monoclinic Double Selenates of the Manganese Group.** A. E. H. TUTTON (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 225—245).—In the group of the series $R_2M(SeO_4)_2,6H_2O$, in which M is manganese, only three salts could be obtained, namely, those in which R is rubidium, cæsium, or ammonium. Potassium manganese selenate, like the corresponding sulphate, only exists in the tetrahydrated form, even at 0°. The morphological relationships between the three salts are similar to those observed in every

other group of the series (cf. A., 1920, ii, 690). The salts al crystallise in the holohedral-prismatic class of the monoclinic system. Rubidium manganous selenate, $Rb_2Mn(SeO_4)_2,6H_2O$, $a:b:c=0·7422:1:0·5008$; $\beta=105° 9'$; $d_4^{20}$ 2·763. Cæsium manganous selenate, $Cs_2Mn(SeO_4)_2,6H_2O$, $a:b:c=0·7319:1:0·4957$, $\beta=106° 22'$; $d_4^{20}$ 3·008. Ammonium manganous selenate, $(NH_4)_2Mn(SeO_4)_2,6H_2O$, $a:b:c=0·7427:1:0·4979$; $\beta=106° 16'$; $d_4^{20}$ 2·158. The ammonium salt, besides the cleavage parallel to $\{\bar{2}01\}$ common to the series, exhibits an even more perfect one parallel to $\{010\}$. The optical constants of the crystals of all the salts were measured. E. H. R.

**Equilibria in the Systems Iron–Carbon–Oxygen and Iron–Hydrogen–Oxygen, and the Free Energies of the Oxides of Iron.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 975—998).—A theoretical paper in which the data obtained by a number of authors in connexion with the two systems named in the title have been correlated and criticised. A number of calculations have been made from the correlated data, and the following conclusions drawn. Ferric oxide and ferroso-ferric oxide at 1100° and above form a continuous series of solid solutions, although there are indications that at temperatures much below 1000° they may not be soluble in each other in all proportions. Ferroso-ferric oxide and ferrous oxide up to 1100° at least definitely do not form a continuous series of solutions, although they do dissolve in each other to a limited extent. Ferrous oxide appears to be soluble in iron to the extent of 20—25 mol.% (6—8% oxygen), although metallic iron is not appreciably soluble in the oxide. Ferrous oxide is unstable with respect to ferroso-ferric oxide and iron below about 565°, and ferroso-ferric oxide shows an inversion point in the same region. When carbon monoxide reacts with pure iron in a closed tube above 500°, carbon is not ordinarily deposited as a separate phase. At temperatures above 800°, a trivariant equilibrium with iron containing dissolved carbon or carbide as the solid phase may be established, or one in which the solid phase contains dissolved oxygen as well as carbon, and the gas is richer in carbon dioxide than in the former case. It is possible that bivariant equilibria corresponding with these, with a separate dissolved carbon or carbide phase, may also be established on repeated treatment, but this does not appear to be proved. With a stream of carbon monoxide acting on iron in the vicinity of 650°, separate phases consisting of carbon, ferrous oxide, and iron containing dissolved oxygen and carbon (or carbide) are probably formed. At higher temperatures, the oxide and separate carbon phases do not appear, and the amount of dissolved carbon decreases. Carbon dioxide acting on iron in a closed tube probably produces again a trivariant system. At temperatures in the neighbourhood of 600° and lower, carbon is present in the solid phase, decreasing in amount as the temperature is increased. The individual results, of the investigators of univariant and bivariant equilibria involving iron or ferrous oxide, ferrous oxide or ferroso-ferric oxide, carbon

monoxide, carbon dioxide, and carbon under conditions such that the presence of separate and definite solid phases in large amounts was assured, are in sufficient agreement to permit the use of equilibrium constants and free energies based on them. These constants are tabulated for the range 600—1000°. Bivariant equilibria involving iron or ferrous oxide, ferrous oxide or ferroso-ferric oxide, and hydrogen yield such different results that the data cannot be safely used. J. F. S.

**The Penetration of Tempering in Steel.** GEORGES CHARPY and LOUIS GRENET (*Compt. rend.*, 1922, **174**, 1273—1276).—A square bar of the steel to be examined is used for the purpose. It is heated in the furnace at the required temperature until its temperature is uniform. The upper part of the bar is then wrapped round with asbestos, and on to the base is directed a regulated stream of cold water. When the cooling is complete, the hardness is determined on one face at different distances from the base. The bar may then, if necessary, be submitted to further thermal treatments and the other three faces used for determining the hardness. The results are in accord with those obtained on a fragment of metal cut out from a thick piece after its tempering. With a nickel–chrome steel, the hardness was found to vary from 387 at 3 mm. from the base to 180 at 90 mm. With an auto-tempering steel, after tempering at 800°, the hardness was practically uniform along the whole length of the bar.

The method may also be used for metals which are not homogeneous, and permits of a study of the influence of cementation on thick plates. In this way, it was found that, in certain cases, the hardness of the part situated behind the cemented region is less than that obtained with a bar of the same composition, tempered under the same conditions, but showing no cemented region. W. G.

**Centrifugal Method for Preparing Colloidal Ferric Hydroxide, Aluminium Hydroxide, and Silicic Acid.** RICHARD BRADFIELD (*J. Amer. Chem. Soc.*, 1922, **44**, 965—974).—Colloidal ferric hydroxide, aluminium hydroxide, and silicic acid may be prepared from the freshly formed precipitates of these substances by removing the excess of precipitating agent by a very thorough washing, which is achieved by means of a centrifuge with a rotation of 32,500 per minute. This method has many advantages over the older methods, chief of which are, (*a*) the removal of the electrolytes formed on precipitation is more complete; (*b*) the addition of a peptising agent and its consequent incomplete removal by either prolonged boiling or dialysis is unnecessary; (*c*) sols of a more uniform degree of dispersion can be prepared, since particles of similar size and of similar degrees of hydration are deposited in the same zone of the centrifuge bowl; (*d*) sols of any desired concentration from a semi-gel to the merest trace can be prepared by the addition of water to the more concentrated form, and all concentrations are very stable. It is shown that aluminium hydroxide

precipitated by ammonium hydroxide in the presence of an exce of sulphate ions is not irreversible. J. F. S.

**The Reduction of Oxides by Hydrogen.** E. BERGER (*Comp rend.*, 1922, **174**, 1341—1343; cf. A., 1914, ii, 656; Sabatier ar Espil, A., 1914, ii, 276).—From a study of the velocity curves f the reduction, by hydrogen, of specimens of nickel oxide prepar in different ways, the author finds that the discontinuity in t curves occurs at different stages in the reduction varying with t specimen. This discontinuity cannot, therefore, be explained c the basis of the formation of an intermediate oxide, and doubt therefore cast on the existence of sub-oxides of nickel. W. G.

**New Properties of the Green Chromium Sulphate.** A RECOURA (*Compt. rend.*, 1922, **174**, 1460—1463).—It has bee shown by Colson (A., 1907, ii, 177, 267, 474) that the green chromiu sulphate, immediately after its solution in water, exists in a con densed form, which is slowly depolymerised. In this condense form, it is found to be capable of masking the sulphate ion in othe sulphates to the extent of several hundred molecules for eac molecule of the green sulphate present. The number of molecule which can be thus masked depends on the length of time durin which the green sulphate has been in solution, the acidity, and th concentration of the solution. W. G.

**X-Ray Examination of the Trioxides of Tungsten, Molybdenum, and their Hydrates.** H. C. BURGER (*Z. anorg. Chem.*, 1922, **121**, 240—242).—The highest oxide of tungsten, $WO_3$, can exist in various forms as large, bright yellow crystals, or long, thin, dark blue, or green needles. All these modifications gave identical angles of reflection which were, however, different from that of the hydrate. This proves that the hydrate is a definite chemical compound with its own characteristic crystal form. It corresponds in composition with $WO_3,H_2O$, that is, $H_2WO_4$; this, on heating, loses water and gives the above trioxide. A definite chemical compound was also indicated in the case of the other hydrate, $WO_3,2H_2O$; that is, $H_4WO_5$ tungstic acid. In the case of molybdenum, the existence of $H_2MoO_4$ as a definite chemical compound was proved. This is a much more convenient method for the solution of such problems than that of measuring the vapour pressure as a function of the composition. The phases in the mixture can be found and the whole work carried out in a short time with a few mg. of the substance. W. T.

**The Valency of Tungsten and Molybdenum in their Complex Octacyanides.** OSCAR OLSSON COLLENBERG (*Z. anorg. Chem.*, 1922, **121**, 298—312).—The author reviews previous work on the subject and shows the sources of error. He determined the valency by means of ammoniacal silver chloride and found that the central atoms were in each case quadrivalent in agreement with their formulæ, $[W(CN)_8]K_4$ and $[Mo(CN)_4]K_4$. These results were confirmed by another method, using ferric sulphate and potassium

permanganate, this method, due to Friedheim and Hoffmann (A., 1902, ii, 265), being modified and so rendered applicable in the presence of cyanides. W. T.

**The Chlorides of Bivalent Molybdenum, Tungsten, and Tantalum. I.** KURT LINDNER [with EMMA HALLER, HERBERT HELWIG, ANTONIE KÖHLER, and HELLMUTH FEIT] (*Ber.*, 1922, **55**, [*B*], 1458—1465).—The formulæ $HMo_3Cl_7,4H_2O$, $HW_3Cl_7,4{\cdot}5H_2O$, and $Ta_6Cl_{14},7H_2O$ have been ascribed by Rosenheim and Kohn (A., 1910, ii, 300), Hill (A., 1917, ii, 36), and Chapin (A., 1910, ii, 303), respectively, to the dichlorides of molybdenum, tungsten, and tantalum. The preparation of these chlorides has been subjected to exhaustive investigation. It is shown that they are uniformly constituted in accordance with the general formula, $HX_3Cl_7,4H_2O$, in which the metal is bivalent. The methods used in their preparation are the treatment of the metals with gaseous chlorine under suitable conditions of temperature and pressure and the reduction of the higher chlorides by gases or other reducing agents such as metals.

At all temperatures up to 1200°, molybdenum is converted by chlorine into the pentachloride. The dichloride is obtained conveniently by passing carbonyl chloride over powdered molybdenum at 700—800°; a small quantity of the pentachloride sublimes, after which the metal gradually becomes coated with a heavy yellow layer of molybdenum dichloride, which ultimately protects the metal from further action. The dichloride is then extracted with concentrated hydrochloric acid and the residual metal is again treated with carbonyl chloride. The compound, $HMo_3Cl_7,4H_2O$, separates almost quantitatively from the acid solutions in the form of long, yellow needles. At about 600°, molybdenum trichloride is the main product of the action of carbonyl chloride on molybdenum, whereas below this temperature the pentachloride is produced. Less favourable but useful results are obtained by the reduction of molybdenum pentachloride with finely divided aluminium in the presence of ignited quartz powder (to moderate the violence of the reaction). The product is subsequently extracted with hydrochloric acid. The yield is considerably diminished by the reduction of molybdenum pentachloride to other stages and even to metallic aluminium and the consequent difficulty of working up the residues.

Tungsten dichloride cannot be prepared from the metal and carbonyl chloride, which, over a wide interval of temperature, give carbon and the "red oxychloride," $WOCl_4$, in addition to small quantities of tungsten hexachloride and probably of tungsten pentachloride. The reduction of tungsten hexachloride by sodium amalgam (Hill, *loc. cit.*) is uncontrollable, and even if successful only gives minimal quantities of the dichloride; the results with an alloy of sodium and potassium are even less promising. On the other hand, tungsten hexachloride is readily reduced to the dichloride by ignition in a stream of nitrogen with powdered aluminium and quartz; the product is extracted with hydrochloric acid and the

reddish-yellow extract is concentrated and saturated with hydrog chloride, thus causing the separation of the compound

$$HW_3Cl_7,4H_2O$$

in slender, yellow needles, which are considerably less stable th the corresponding molybdenum compound and rapidly lose hydrog chloride when exposed to air.

Tantalum is converted into its pentachloride by carbonyl chloric Tantalum pentachloride is reduced by powdered metals to t dichloride and, since the reaction proceeds less violently than wi the molybdenum and tungsten compounds, the addition of powder quartz may be omitted. Aluminium, zinc, and lead are efficie The residues are extracted exhaustively with hydrochloric aci The isolation of the compound $HTa_3Cl_7,4H_2O$, a blackish-gree unusually stable, crystalline powder, from the extracts is a matt of some difficulty, since it only separates from very concentrat solutions and its crystallisation is greatly impeded by the preser of dissolved aluminium chloride. It is preferable, therefore, to zinc which can be removed as sulphide after addition of sodi acetate to the solution or lead, the dissolved traces of which c be precipitated directly with hydrogen sulphide. Molten tantal pentachloride cannot be reduced electrolytically between cark poles, since the substance is an insulator (cf. Biltz and Voigt, t vol., ii, 302). Electrolysis takes place after addition of alk chlorides, and the dichloride is formed to some extent; the meth has no preparative value. H. W

**Electrolytic Removal of Alkali from Salts.** A. LOTTI MOSER (*Kolloid Z.*, 1922, **30**, 346—348).—The author shows tl by the electrolysis of normal sodium tungstate it is possible prepare paratungstates and other complex tungstates by removal of sodium hydroxide. In the case of sodium paratu state, the preparation is carried out as follows. A solution normal sodium tungstate ($Na_2WO_4,2H_2O$), 51 grams in 200 of water, is placed in a 250 c.c. porous pot which stands in a beal containing exactly 750 c.c. of *N*/10-sodium hydroxide. An anc consisting of a coil of platinum wire is placed in the porous c and the electrolysis carried out with a current of 2 amperes until sodium hydroxide has increased in concentration by the calcula amount. When this state is reached, the anode solution is allow to crystallise; sodium paratungstate separates in large, vitre crystals. In the same way, sodium ditungstate and metatungst were also prepared (cf. Kröger, this vol., ii, 212). J. F. S

**The Hydrates of Uranium Tetroxide and Uranium Trioxi** GUSTAV F. HÜTTIG and EDITH VON SCHROEDER (*Z. anorg. Che* 1922, **121**, 243—253).—Details are given of the preparation the bright yellow, hygroscopic hydrate of uranium tetroxide, wh corresponds with the formula $UO_4,3H_2O$. This was heated ir vacuum, but the tetroxide, $UO_4$, could not be obtained, the final p ce ct being the trioxide, $UO_3$. The compound loses oxygen bef the the water is expelled, and the authors consider the existence confi etroxide as very doubtful. The changes in composition w

studied in a Hüttig tensi-eudiometer (A., 1921, ii, 195), and the following hydrates were indicated: $UO_4,4{\cdot}5H_2O=UO_3,H_2O_2,3{\cdot}5H_2O$; $UO_{3{\cdot}5},3H_2O=UO_3,0{\cdot}5H_2O_2,2{\cdot}5H_2O=H_2U_2O_8,5H_2O$; $UO_{3{\cdot}5},2H_2O=UO_3,0{\cdot}5H_2O_2,1{\cdot}5H_2O=H_2U_2O_8,3H_2O$[?]; peruranic acid pentahydrate, $UO_3,0{\cdot}5H_2O=H_2U_2O_7$, pyrouranic acid. It is assumed that *these are derivatives of the trioxide and that hydrogen peroxide is* contained in the first, second, and third compounds.

In the case of uranium trioxide, indication was given of the following hydrates: $UO_3,2H_2O=H_2UO_4,H_2O$, $UO_3,H_2O=H_2UO_4$, uranic acid. W. T.

**The Triboluminescence of Uranium Salts and Three New Organic Uranium Compounds.** J. A. SIEMSSEN (*Chem. Ztg.*, 1922, **46**, 450; cf. A., 1919, ii, 346).—A specimen of uranium nitrate which had been kept in a stoppered bottle for forty-one years showed weak triboluminescence compared with other preparations, and its luminosity was very slight. A specimen of sodium uranate which was not triboluminescent was converted into uranium nitrate which showed fairly strong triboluminescence. A preliminary announcement is made of the discovery of three salts, obtained by the action of pyrazolone derivatives on uranium compounds, which possess powerful bactericidal properties. No further chemical particulars are given. E. H. R.

**The Behaviour of the Stannic Acids towards Hydrochloric Acid.** GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1922, **121**, 1122—1133).

**The Anodic Corrosion of Bismuth. Bismuth Compounds.** E. B. R. PRIDEAUX and H. W. HEWIS (*J. Soc. Chem. Ind.*, 1922, **41**, 167—171T).—As a possibly advantageous alternative to attack by nitric acid, the anodic corrosion of bismuth in an anolyte of sodium nitrate was investigated. The bismuth anodes were cast on copper wire, the cathode was a strip of nickel and in order to prevent reduction of the nitrate to ammonia it was placed in a catholyte of dilute alkali in a porous pot.

In the first series of experiments, 10% sodium nitrate solutions were used, with a current density of 12·5 amperes per sq. dcm. and an average of 4·6 volts. The current efficiency calculated from the anodic loss was 100%, and 1·76 kilowatt-hours were consumed per kilo. of bismuth dissolved. The product was an oxynitrate containing on the average about 30% of bismuth oxide, and came down partly as a white deposit and partly as a crust on the anode. The amount of bismuth in the solution was negligible. In the second series of experiments, saturated solutions of sodium nitrate were used as the anolyte, and in this case the bismuth oxynitrate came down entirely as a loose precipitate, and one-half to three-quarters of the total bismuth remained in solution, from which it may be obtained as oxynitrate by dilution, or used directly for other bismuth preparations. The fully hydrated white bismuth hydroxide, $Bi(OH)_3$, can be prepared from this anodic solution by allowing it to run into an equal volume of $N/2$-sodium hydroxide

diluted about five times. The white precipitate is washed by decantation. An examination of xeroform (bismuth tribromophenoxide) prepared by the usual method of adding bismuth nitrate to a solution of tribromophenol in sodium hydroxide showed that it contained an appreciable quantity of oxynitrate and the alcoholic extract contained nitrobromophenols in addition to much tribromophenol. On ignition, moreover, it gave a lemon yellow residue containing bromine, and it does not therefore yield pure bismuth oxide, as usually stated. Commercial xeroform appears therefore to be very impure, although doubtless quite suitable for the purpose intended. A purer preparation was obtained by using the anodic solution of bismuth nitrate in sodium nitrate. It forms a bulky, pink precipitate, which, although it has a definite bismuth content (15·46%), does not appear to correspond exactly with any of the simpler compounds which might be expected for example, $(C_6H_2Br_3O)_3Bi$ requires 17·36%. It is possibly a hydrate, and the matter is being further investigated. G. F. M.

**Double Haloids of Bismuth and Thallium.** G. Canneri and G. Perina (*Gazzetta*, 1922, **52**, i, 241—246; cf. this vol., ii, 378; Ephraim and Barteczko, A., 1909, ii, 236).—*Bismuth thallous bromide*, $2TlBr,BiBr_3$, prepared by dissolving bismuth carbonate in nitric acid and adding potassium bromide, crystallises in lustrous, lemon-yellow, hexagonal lamellæ, and in neutral aqueous solution undergoes rapid hydrolysis to thallous bromide, bismuth oxybromide, and bromine. *Bismuth thallous iodide*, $2TlI,BiI_3$, prepared by adding potassium iodide to an acid solution containing thallium and bismuth, forms red, regular hexagonal plates, exhibits physical and chemical properties similar to those of the preceding compound, and is soluble in about 20,000 parts of water.

The formation of this insoluble double iodide may be used as a means of detecting and estimating bismuth after other metals forming insoluble iodides have been removed. A solution containing 0·029 gram of bismuth per litre yields a voluminous red precipitate with a thallous salt and potassium iodide, whereas with hydrogen sulphide only a faint brown coloration is obtained. For the estimation, the solution of the bismuth salt is acidified with hydrochloric acid and then treated with a known volume, in excess, of standard potassium iodide solution. Standard thallous sulphate solution is next run in from a burette until precipitation of the red double iodide ceases and that of yellow thallous iodide is evident. The precipitate is collected on a Gooch crucible and washed thoroughly with absolute alcohol, the residual excess of potassium iodide in the solution being estimated by means of potassium iodate. If $a$ represents the amount in grams of iodine added as iodide to the solution, $b$ that combining with the thallium, and $c$ that remaining in excess, calculated on the basis that 3 atoms of iodine correspond with 1 atom of bismuth, the weight of the latter in grams is given by: $208[a-(b+c)]/380·76$.

Addition to a solution of $K_3Bi(CNS)_6$ (cf. Vanino and Hauser, A., 1902, i, 14) of a proportion of thallium acetate corresponding

th one equivalent of the potassium results in the formation of orange-yellow *precipitate* of the composition $K_2TlBi(CNS)_6$, ilst with double this proportion of thallium acetate, the *com- und*, $KTl_2Bi(CNS)_6$, is obtained as a paler yellow precipitate. l attempts to prepare the trisubstituted salt, $Tl_3Bi(CNS)_6$, have oved unsuccessful, the molecule undergoing demolition with ·mation of thallous thiocyanate. T. H. P.

**The Reduction of Tantalum Pentachloride.** OTTO RUFF d FRITZ THOMAS (*Ber.*, 1922, **55**, [*B*], 1466—1473).—Tantalum ntachloride is reduced by metallic aluminium in the presence aluminium chloride at 300° to a mixture of various chlorides of ntalum. A larger excess of aluminium remains unchanged even hen, as is occasionally the case, metallic tantalum is formed. ne temperature is limited by the resistance of the tubes. The ırk green product of the reaction evolves aluminium chloride ıd tantalum pentachloride when heated, the latter being given f in such a manner that the composition of the residue can be gulated by the choice of temperature and pressure. A mixture orresponding approximately with tantalum tetrachloride is otained at 250°/2—3 mm.; at 350—400° the residue has the omposition of a trichloride which is itself decomposed at about 00°, leaving a mixture of di- and tri-chlorides.

The mixtures of chlorides are moderately stable towards air. 'reatment with water causes the formation of intensely green olutions of the trichloride, whilst the pentachloride is hydro- ysed to hydrochloric and tantalic acids and the dichloride remains ndissolved as a blackish-green residue. The green solutions ecome oxidised slowly on exposure to air, the action being checked y the presence of acids. The di- and tri-chlorides are soluble in old, sufficiently dilute sodium hydroxide solutions without evolu- ion of hydrogen or alteration in the valency of the element. The lkaline solutions are oxidised with unusual readiness by air and volve hydrogen when they are warmed; a brown tantalous oxide s thereby produced as an intermediate step in the formation of antalic acid. The production of this substance is also observed luring rapid oxidations (with hydrogen peroxide or nitric acid) n acid solution. When oxidation is effected by hydrogen peroxide n alkaline solution, a brown solution of a pertantalate is obtained which evolves oxygen and becomes colourless when boiled.

The behaviour of aqueous solutions of titanium trichloride towards common reagents is described in detail. H. W.

**Gold Sulphides.** A. GUTBIER and E. DÜRRWÄCHTER (*Z. anorg. Chem.*, 1922, **121**, 266—274).—Various sulphides of gold are described in the literature. The authors could not obtain the sulphides with the formulæ $Au_2S$ and $Au_2S_2$. A rapid stream of hydrogen sulphide passed at the ordinary temperature into a 2% solution of chloroauric acid, $[AuCl_4]H$, in *N*-hydrochloric acid gave a black precipitate of auric sulphide, $Au_2S_3$, mixed with small amounts of metallic gold. The relative amounts of sulphide and metal depend on temperature, concentration of the chloro-

auric acid, and the rate of passing in the hydrogen sulphide. low temperatures $-2°$, with a low concentration of the chlo acid and a very rapid stream of gas, the pure sulphide was obtain The low concentration of the tetrachloro-acid is necessary, beca it reacts with the sulphide formed. Auric sulphide reacts m rapidly with auric chloride than with the tetrachloro-auric a and pure auric sulphide is not obtained as above if the gas is bubb into a solution of auric chloride. W. T.

**Some Complex Chlorides containing Gold. III. A Ne Cæsium Auric Chloride.** HORACE L. WELLS (*Amer. J. Sc* 1922, [v], **3**, 414—416).—This salt, $Cs_5Au_3Cl_{14}$, was obtained fr a concentrated solution of cæsium chloride containing compa tively little auric chloride. It is best prepared in the presence concentrated hydrochloric acid, because it is quickly decompos by water, with the formation of a yellow precipitate of the usu double salt, $CsAuCl_4$. The new complex salt was obtained very minute deep red crystals. W. T.

**Rubidium (Cæsium) Silver Gold Bromides.** EUGE SUSCHNIG (*Monatsh.*, 1921, **42**, 399—404).—Triple bromides rubidium (or cæsium), silver, and gold have been prepared corr sponding with the triple chlorides described by Bayer (A., 192 ii, 688) and discussed by Emich (*ibid.*, 689). The silver and gol are vicarious constituents, and their proportions in the compoun depend on their concentrations in the solutions from which crysta lisation takes place. The compounds correspond with the formul $Rb_3Ag_xAu_{(2-x/3)}Br_9$ and $Cs_3Ag_xAu_{(2-x/3)}Br_9$. In the rubidium con pound, the atomic proportion of silver varied from 0·77 to 1·5 and in the cæsium compound from 0·89 to 1·14. The rubidiu salt forms almost black needles, deep violet in thin sections, whil the cæsium salt is similar to Bayer's triple chloride. The sal can only be prepared in strong hydrobromic acid solution; the are decomposed by water. An analogous potassium salt coul not be obtained, but microscopical tests showed that an ammoniu compound is formed, and also compounds with organic base such as guanidine, caffeine, pyridine, hexamethylenetetramine and methyl- and ethyl-amine instead of rubidium or cæsium The compounds are adapted to the microchemical identificatio of gold, silver, and rubidium or cæsium in absence of disturbin elements. Microchemical tests indicate that aluminium, chromium zinc, nickel, cobalt, uranium, mercury, and manganese can replac silver in the triple chlorides and that ferric iron, calcium, strontium and barium can replace the alkali metal. E. H. R.

**Determination of the Werner Structure of Inorgani Compounds by means of X-Rays.** PAUL SCHERRER and P STOLL (*Z. anorg. Chem.*, 1922, **121**, 319—320).—The space lattice of the following complex salts were determined: $[PdBr_6]Rb_2$, $[Ni(NH_3)_6]Cl_2$, and $[PtCl_6]K_2$. The six co-ordinated groups were placed at the six corners of a regular octahedron with the centra atom at the centre. The salts resembled calcium fluoride with

the co-ordinated complex taking the place of the atom calcium. The platinum and chlorine were $1{\cdot}6\times10^{-8}$ cm. apart and the edge of the octahedron measured $9{\cdot}7\times10^{-8}$ cm. W. T.

**Chloroiridiates of Complex Metal Bases.** A. BENRATH, W. BÜCHER, and H. ECKSTEIN (*Z. anorg. Chem.*, 1922, **121**, 347—360).—Jörgensen prepared a large number of salts of the ammines of cobalt and chromium by combining the complex bases with different acid radicles. The complex acids of the noble metals formed beautifully coloured, crystalline salts. The present authors employed the complex hexachloroiridiate as the acid radicle. The salts formed with cobalt as the central atom of the complex base were found to crystallise only with difficulty and to be more unstable than the corresponding platinum compounds. In the hexammine salts the most stable were those in which all the acid radicles were replaced by the complex iridium radicle; the others were very unstable. The hexammine and pentammine salts as well as the aquo-salts with four or five molecules of ammonia are insoluble, stable, yellow to brown in colour, decomposed only by long boiling with an alkali hydroxide, micro-crystalline and decomposed when heated alone at 150°. The tetrammine salts are more soluble, can be precipitated with alcohol, are crystalline and golden-yellow to bronze-red in colour. They decompose in hot water, and when heated alone at 105—120°. The preparation and properties of the following are described: Hexamminecobaltic hexachloroiridiate, $[Co(NH_3)_6]_2[IrCl_6]_3$. Hexamminecobaltic nitrate hexachloroiridiate, $[Co(NH_3)_6]NO_3[IrCl_6]$. Basic hexamminecobaltic hexachloroiridiate, $[Co(NH_3)_6]OH[IrCl_6]$. Chloropentamminecobaltic hexachloroiridiate, $[Co(NH_3)_5Cl][IrCl_6]$. Aquopentamminecobaltic hexachloroiridiate, $[Co(NH_3)_5H_2O]_2[IrCl_6]_3$. *trans*-Dinitrotetramminecobaltic hexachloroiridiate trihydrate,

$$[Co(NH_3)_4(NO_2)_2][IrCl_6],3H_2O.$$

*cis*Dinitrotetramminecobaltic hexachloroiridiate,

$$[Co(NH_3)_4(NO_2)_2][IrCl_6].$$

*cis*Dichlorotetramminecobaltic hexachloroiridiate,

$$[Co(NH_3)_4Cl_2]_2[IrCl_6].$$

Aquonitrotetramminecobaltic hexachloroiridiate,

$$[Co(NH_3)_4(H_2O)NO_2][IrCl_6].$$

The salts with chromium in the basic complex resemble the corresponding cobalt compounds. They are dirty yellow in colour. The hexammine and pentammine salts separated as very fine suspensions, the tetrammine salts crystallised much more readily. The following salts are described: Hexamminechromic hexachloroiridiate, $[Cr(NH_3)_6]_2[IrCl_6]_3$. Hexamminechromic nitrate hexachloroiridiate, $[Cr(NH_3)_6]NO_3[IrCl_6]$. Basic hexamminechromic hexachloroiridiate, $[Cr(NH_3)_6]OH[IrCl_6]$. Hexamminechromic sulphate hexachloroiridiate, $[Cr(NH_3)_6]_2(SO_4)_2[IrCl_6]$. Chloropentamminechromic hexachloroiridiate, $[Cr(NH_3)_5Cl][IrCl_6]$. Hydroxoaquotetramminechromic hexachloroiridiate, $[Cr(NH_3)_4(H_2O)OH][IrCl_6]$. Dithiocyanatotetramminechromic hexachloroiridiate,

$$[Cr(NH_3)_4(CNS)_2]_2[IrCl_6].$$

Dichloroaquotriamminechromic hexachloroiridiate,

$[Cr(NH_3)_3H_2OCl_2]_2[IrCl_6]3H_2O$.

The nitrate iron could not be separated from the chloroiridiate ion by means of nitron as the complex ion also forms an insoluble product, thus resembling the chloro-acids of the other noble metals. The compound, $(C_{20}H_{16}N_4)_2[IrCl_6]H_2$, separates as a dark red crystalline precipitate. Ruthenium can be partly separated from the other noble metals by fractional crystallisation of the nitrous compounds, that of ruthenium being more soluble than the others.

W. T.

## Mineralogical Chemistry.

**Calcium Uranium Autunites.** F. HENRICH (*Ber.*, 1922, **55** [*B*], 1212—1215; cf. A., 1918, ii, 96).—The detailed analysis is recorded of a calcium uranium autunite from Steinbruch Fuchsbau near Leopoldsdorf, in the Fichtelgebirge, the analysis (I) of which agrees closely with the formula $CaO,(UO_3)_2,P_2O_5,10H_2O$. The ratio of radium to uranium is $2{\cdot}8\times10^{-7}$, or 87% of the equilibrium value between the two elements. This appears to be the highest value yet recorded for a calcium uranium autunite. A Portuguese calcium uranium autunite from the Beira Alta Province (analysis II) had a ratio of radium to uranium which is only 38% of the theoretical value and was appreciably poorer in radium than the Bavarian specimen.

| | $UO_3$. | CaO. | $P_2O_5$. | Insol. | Ignition. | Total. |
|---|---|---|---|---|---|---|
| I. | 59·71 | 5·92 | 14·30 | 1·50 | 18·17 | 99·6 |
| II. | 60·72 | 6·04 | 14·55 | 0·53 | 18·27 | 99·93 |

H. W.

**Ceruleofibrite, a New Mineral.** EDW. F. HOLDEN (*Amer. Min.*, 1922, **7**, 80—83).—As radiating tufts of bright-blue fibres and as blackish-blue, fibrous masses, this was found on specimens of cuprite from Bisbee, Arizona. The needles are orthorhombic ($a:b:c=0{\cdot}78:1:0{\cdot}49$) with angles near to those of brochantite; *d* 3·54, H. 3. The optical characters are stated. The mineral is readily soluble in cold dilute hydrochloric acid. Analysis gives the formula $CuCl_2,\frac{1}{3}Cu_3As_2O_8,6Cu(OH)_2$, representing a very basic chloroarsenate.

| CuO. | Cl. | $As_2O_5$. | $H_2O$. | Insol. | Total less O for Cl. |
|---|---|---|---|---|---|
| 73·8 | 7·5 | 7·5 | 11·7 | 0·3 | 99·1 |

L. J. S.

**Chemical Investigation of Japanese Minerals containing Rarer Elements. IV. Samarskite and an Unnamed Mineral from Ishikawa, Iwaki Province.** YÛJI SHIBATA and KENJIRÔ KIMURA (*J. Chem. Soc. Japan*, 1922, **43**, 301—312; cf. this vol., ii, 220).—Samarskite, *d* 5·50, hardness 5—6, from Ishikawa-machi, Iwaki Province, gave on analysis :

| MgO. | CaO. | MnO. | FeO. | $Al_2O_3$. | Rare earths. | $UO_2$. | $SnO_2$. | $TiO_2$. | $SiO_2$. | $Cb_2O_5$. | $Ta_2O_5$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·25 | 1·25 | 0·84 | 9·64 | 0·61 | 17·34 | 16·87 | 0·73 | 0·10 | 0·37 | 41·11 | 10·00 | 0·85 | 99·96 |

From which is deduced the formula $2[M_2(Cb,Ta)_2O_7],R_2(Cb,Ta)_2O_8$, where M=Fe, Ca, Mg, Mn, UO, and R rare earth metals.

On spectroscopic examination, lines of lead, barium, strontium, tungsten, yttrium, erbium, dysprodium, gadrinium, samarium, scandium, and terbium were observed.

Imperfect black crystals, with resinous lustre of an unnamed mineral (*d* 6·2—6·4, hardness 5—6, streak, blackish-brown) from the same locality gave on analysis :

| MgO. | CaO. | MnO. | FeO. | $Al_2O_3$. | Rare earths. | $UO_2$. | $SnO_2$. | $SiO_2$. | $TiO_2$. | $Cb_2O_5$. | $Ta_2O_5$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *1·07* | *0·86* | *0·40* | *11·78* | *0·87* | *8·40* | *21·88* | *1·20* | *0·30* | *0·21* | *36·80* | *15·00* | *0·89* | *99·66* |

On spectroscopic examination, lines of lead, barium, strontium, zinc, copper, bismuth, beryllium, yttrium, erbium, gadrinium, dysprodium, samarium, lanthanum, and scandium were observed.

K. K.

**Composition of Thortveitite from Madagascar.** CH. BOULANGER and G. URBAIN (*Compt. rend.*, 1922, **174**, 1442—1443; cf. *A.*, *1920*, *ii*, *627*; *this vol.*, *ii*, *306*).—*The mean of five analyses is* :

| $SiO_2$. | $Sc_2O_3$. | $ZrO_2$. | $Al_2O_3$. | $Fe_2O_3$. | Gl, Mn, Sn, Sb, Pb. | Total. |
|---|---|---|---|---|---|---|
| 44·1 | 42·4 | 8·4 | 3·3 | 2·0 | traces | 100·2 |

The figures for scandia include about 0·5% of yttrium earths (yttrium, neoytterbium, and lutecium). The mineral is only slightly attacked by hydrofluoric acid or by fused bisulphates. Two or three fusions with sodium carbonate are necessary for its decomposition.

L. J. S.

**Velardeñite from California.** EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1922, **60**, Art. 22, 1—4).—A dull olive-green, coarsely-granular mineral with greasy to resinous lustre, from Tulare Co., California, is colourless under the microscope. It is optically uniaxial and negative, $\omega$=1·657, $\epsilon$=1·653. Analysis I corresponds with $14CaO,2MgO,5Al_2O_3,9SiO_2$, *which is interpreted* as a mixture of five parts of velardeñite ($2CaO,Al_2O_3,SiO_2$) with *two of åkermanite* ($MgO,2CaO,2SiO_2$).

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|
| I. | 27·88 | 25·52 | 1·59 | 0·43 | 40·86 | 4·18 | 0·34 | 100·80 |
| II. | 32·66 | 5·95 | 24·15 | — | 35·51 | 2·59 | — | 100·86 |

Mixed with it are grains of a yellowish-green garnet which (with some spinel) gave analysis II, indicating andradite.

L. J. S.

**White Chlorites.** EARL V. SHANNON and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1922, **12**, 239—241).—Colerainite (*A.*, *1918*, ii, 325) and sheridanite (*A.*, *1912*, *ii*, 1181) are classed as white chlorites. Analysis I is of a white chlorite from Brinton's quarry, Chester Co., *Pennsylvania*, *II from* Nottingham, Chester

Co., and III of a greenish-grey schistose rock from Miles City, Montana. I and III agree with the sheridanite formula

$$3MgO,Al_2O_3,2SiO_2,3H_2O,$$

but II gives the ratios $9MgO,Al_2O_3,6SiO_2,7H_2O$. III agrees also with sheridanite in its optical constants, whilst II is different.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $H_2O-$. | $H_2O+$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 28·10 | 26·20 | 1·66 | nil | trace | trace | 30·36 | 0·56 | 14·00 | 100·88 |
| II. | 36·70 | 10·38 | 1·22 | trace | trace | 0·86 | 36·44 | 1·06 | 13·80 | 100·46 |
| III. | 27·78 | 24·30 | 1·43 | 0·35 | nil | trace | 32·71 | 0·06 | 13·01 | 99·64 |

L. J. S.

**Crocidolite from Eastern Pennsylvania.** EDGAR T. WHERRY and EARL V. SHANNON (*J. Washington Acad. Sci.*, 1922, **12**, 242—244).—Blue pleochroic amphiboles ("glaucamphiboles") occur at many localities in eastern Pennsylvania. Analysis of material from Oley Line shows it to be a semimagnesian crocidolite with the formula $H_2O,Na_2O,MgO,FeO,Fe_2O_3,6SiO_2$.

| $SiO_2$. | $Ti_2O_3$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O-$. | $H_2O+$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 51·62 | 2·27 | 0·92 | 18·36 | 10·93 | 0·48 | 5·92 | 5·62 | 0·66 | 1·04 | 2·57 | 100·39 |

Titanium is regarded as replacing aluminium and iron, rather than silicon, and to it the deep blue is ascribed. The low content of alkalis is accounted for by the replacement of sodium by hydrogen. L. J. S.

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## Analytical Chemistry.

**A New Method of Colorimetry.** PAUL DOSNE (*Bull. Soc. Ind. Mulhouse*, 1922, **88**, 73—77).—A beam of light (from a Nernst lamp or other suitable source) is directed upwards through a column of a solution of known strength of the coloured substance under investigation and the height of the column necessary for the complete absorption of the transmitted light, as observed through a spectroscope, is determined. Since under these conditions the colouring power of a substance is directly proportional to the height of the column and to the strength of the solution, the method allows various colouring matters to be compared when dissolved in water, alcohol, or other suitable solvents. A. J. H.

**Colorimetry.** PAUL FLEURY (*Bull. Soc. Chim. Biol.*, 1922, **4**, 223—232).—A discussion of the conditions under which colorimetric methods yield the most accurate results. E. S.

**Colorimetry.** (MLLE) Y. GARREAU (*Bull. Soc. Chim. Biol.*, 1922, **4**, 233—234).—The accuracy of the colorimetric method is indicated by the concordant results obtained during a large number of estimations of sugar by the picric acid method. E. S.

**Improved Form of Gas-analysis Apparatus.** E. W. Blair [a]d T. Sherlock Wheeler (*J. Soc. Chem. Ind.*, 1922, **41**, 187—[1]8T).—A modification of the usual Bone-Wheeler apparatus is [de]scribed, in which compressed air and reduced pressure are [e]mployed to alter the mercury levels; this saves much of the [la]bour involved in raising and lowering the mercury reservoirs. [T]he pressure of the air supply is about two atmospheres. In other [re]spects, the method of working the apparatus is not altered.

W. P. S.

**The Absorption Meter, an Apparatus for Gas Analysis.** . Moser (*Z. anorg. Chem.*, 1922, **121**, 313—318).—The author [d]escribes a simplification of the apparatus he employed for the [g]ravimetric estimation of hydrogen phosphide (A., 1922, ii, 393). [T]he apparatus has been tested and gives good results in the [e]stimation of sulphur dioxide, cyanogen, hydrogen cyanide, silicon [fl]uoride, the hydrides of arsenic and antimony, ozone, and chlorine. [I]t is unsuitable for carbon dioxide or any gases which requires an [a]bsorption liquid affected by the air (baryta water). W. T.

**Apparatus for Determining Hydrogen-ion Concentration. [A]pplication to the Detection of Mineral Acids in Vinegar.** [A]ndré Kling, A. Lassieur, and (Mme) A. Lassieur (*Ann. [C]him. analyt.*, 1922, **4**, 135—137).—A simple apparatus is described [f]or determining hydrogen-ion concentration electrometrically. It [i]s shown that the hydrogen-ion concentration of vinegars con[t]aining from 5—7% of acetic acid varies from $p_H$ 2·54 to 2·83 and [t]hat the addition of 0·24% of sulphuric acid causes this value to [b]ecome 1·48 to 2·02. W. P. S.

**The Clark Hydrogen-electrode Vessel and Soil Measurements.** Daniel J. Healy and Perry E. Kanaker (*Soil Sci.*, 1922, **13**, 323—328).—Satisfactory measurements of the hydrogen-ion concentration of fresh and air-dried soils can be made with the Clark hydrogen-electrode vessel. Air drying increases the values obtained over those of fresh samples. A. G. P.

**The Estimation of Chlorine in Organic Material.** Stefan von Bogdándy (*Z. physiol. Chem.*, 1922, **120**, 30—41; cf. A., 1913, ii, 426).—The author shows that if his method is carried out according to his instructions, high results are not obtained as is asserted by Gutmann and Schesinger (A., 1914, ii, 379). S. S. Z.

**Application of Amalgams in Volumetric Analyses. III. Estimation of Iodic, Bromic, and Chloric Acids.** Suetarô Kikuchi (*J. Chem. Soc. Japan*, 1922, **43**, 173—177).—Iodic acid reacts at 60° with tervalent titanium obtained by reduction of titanic acid as described previously (A., 1921, ii, 596), the excess of tervalent titanium being then titrated with iron alum. The reaction proceeds as follows: $IO_3' + 6Ti^{\cdots} + 6H^{\cdot} = I' + 6Ti^{\cdots\cdot} + 3H_2O$. Bromic and chloric acids can be estimated by similar procedure.

K. K.

**Sodium Peroxide.** JAROSLAV MILBAUER (*Chem. Listy*, **16**, 84–86).—The estimation of the active oxygen of sodium peroxide b means of acid potassium permanganate solution is examined. Th author finds that the best results are obtained by the additio of boric acid to the solution, as this fixes the hydrogen peroxid liberated by the acid. This method is very exact and rapid, an does not require the use of ice.

The effects produced by the presence of various metallic salts and of spongy platinum and palladium are also investigated. I is found that if the salt is added to the water before the sodiun peroxide, the results for the estimation of oxygen will be low if the salt is added after the solution of the sodium peroxide i water, the results are high. This explains the failure of the us of permanganate solution alone, as the manganous sulphate forme acts as a catalyst, which must be neutralised by an anti-catalys (in this case boric acid).

The iodometric method of Kingzett (T., 1880, **37**, 792) is als examined and found satisfactory.

The influence of catalysts on the method whereby the peroxid is analysed by estimation of the oxygen liberated by its decom position in acid or alkaline solution is also studied. From th results obtained for this, the author formulates, as a method fo the estimation of the active oxygen of sodium peroxide, its decom position in alkaline solution, in the presence of cupric sulphate and the measurement of the gaseous oxygen so liberated. Th advantage of this method over that of Archbutt (A., 1895, ii, 185 is that the decomposition is complete in two minutes, and tha the evolved oxygen is free from carbon dioxide.

By means of these new methods of estimation the author show that the action of the atmosphere on sodium peroxide is principall due to the presence of moisture. R. T.

**Estimation of Sulphur Dioxide.** G. BASIL BARHAM (*Chem News*, 1922, **124**, 279—281).—Titration with permanganate solutio under definite conditions is recommended for the estimation o sulphur dioxide. Dilute sulphuric acid solution is treated with a definite volume of standard permanganate solution, and th mixture then divided into two equal portions; the sulphur dioxid solution under examination is added to one portion and the per manganate solution is added until the coloration is again equa in intensity to that of the other portion, which has been reserved for comparison. To ensure the colorations being of the same tint, the acid solution should be reduced and oxidised once or twice (with sulphite and permanganate solutions, respectively) before it is used for the actual estimation. W. P. S.

**Examination of Foods for the Presence of Sulphites.** A. CHASTON CHAPMAN (*Analyst*, 1922, **47**, 204—205).—When foods containing onions or mustard are acidified with phosphoric acid and distilled in a current of carbon dioxide, the distillate on oxidation with bromine will yield a distinct quantity of sulphuric acid; if the oxidation is made with hydrogen peroxide in place of bromine,

these foods will not yield any sulphuric acid unless they actually contain sulphites. W. P. S.

**Factors Influencing the Estimation of Sulphates in Soil.** C. T. Hirst and J. E. Greaves (*Soil Sci.*, 1922, **13**, 231—249).—A comparison was made between the gravimetric method of estimating sulphates as barium sulphate and the volumetric chromate method. By the latter method an average of 97% of the sulphate in soil extracts could be recovered. Sodium and potassium chlorides had little effect on the results obtained; but in the presence of iron and aluminium salts the volumetric method tended to give low results. The presence of nitrates caused high figures by the gravimetric method and low ones by the volumetric method. A 1 : 5 water extract of the soils used, was found to be sufficient to remove all sulphates after forty minutes' shaking. Soils particularly rich in gypsum needed shaking with water for a longer period. Extracts should be clarified by a Pasteur-Chamberland filter.

Very small quantities of sulphates can be detected more easily by the chromate than by the gravimetric method. A. G. P.

**The Analysis of Polythionates.** Albin Kurtenacker and Albert Fritsch (*Z. anorg. Chem.*, 1922, **121**, 335—343).—The authors have already found that tetrathionates react quantitatively with a cyanide to form thiosulphates (A., 1921, ii, 502). Trithionates were found by Raschig (A., 1920, ii, 756) to react quantitatively with cyanides in hot alkaline solutions to form sulphites. The latter reaction is incomplete in neutral solutions, whereas tetrathionates in alkaline solutions give sulphites as well as thiosulphates. This reaction is therefore unsuitable for the estimation of a mixture of these two polythionates. The estimation of a mixture of polythionates by means of a sulphite as recommended by Raschig was found to be unsatisfactory. The method of Riesenfeld and Feld (this vol., ii, 45) was tested. In the absence of other polythionates, the trithionate reacts quantitatively with copper sulphate, but the estimation is not applicable to mixtures. A tetrathionate boiled for half an hour with copper sulphate gave a precipitate of copper sulphide and sulphur in proportions corresponding with the decomposition of the tetrathionate as follows: $S_4O_6''=S_3O_6''+S$. The authors found, contrary to the results of Riesenfeld and Feld, that tetrathionates were quite stable; a solution showed no decomposition after keeping for fourteen days, the instability reported being due to impurities. W. T.

**Pregl's Microanalysis.** Friedrich Holtz (*Ber.*, 1922, **55**, [*B*], 1496—1497).—The use of a bomb furnace in the estimation of halogen and sulphur is avoided by placing the tubes in brass tubes which are closed at one end and stoppered at the other and are heated in the vapour of boiling diphenylmethylamine, b. p. 295°.

The estimation of nitrogen in difficultly-combustible substances is effected in silica tubes which are filled in the following order: asbestos plug, oxidised copper wire (7 cm.), reduced copper wire

(11 cm.), asbestos plug, copper oxide powder mixed with th substance and a little potassium chlorate (4 cm.), oxidised coppe wire (5 cm.). The tube is supported at either end on gutters line with asbestos in such a manner that the portion of the tuhe con taining the reduced copper is left exposed to the direct heat of th burner. This portion of the tube is doubly protected on its uppe side. After displacement of the air by carbon dioxide, the reduce copper is raised to a white heat and after a second passage of carbo dioxide the heating of the remainder of the tube is effected ver gradually in the direction towards the reduced copper. In thi manner, the decomposition of the oxides of nitrogen is effecte with certainty.

Substances may be conveniently dried in a hollow copper cub the walls of which are 1 cm. thick and 6·5 cm. long internally.

H. W.

**A "Micro-Kjeldahl" Method of Estimating Nitrogen** ARTHUR R. LING and WILLIAM JOHN PRICE (*J. Soc. Chem. Ind.* 1922, **41**, 149—151T).—A weighed portion of the substance con taining 1·0—0·1 mg. of nitrogen is boiled until colourless witl 8 c.c. of concentrated sulphuric acid, 1 gram of dry potassiun sulphate, 0·02 gram of anhydrous copper sulphate, and 2 drop of 2·5% platinic chloride solution. After cooling and diluting with 15 c.c. of water, the liquid is distilled from a 300 c.c. flasl with sufficient 40% sodium hydroxide solution to render it alkaline and the ammoniacal distillate is collected in 50 c.c. of water in a graduated 250 c.c. flask. All the ammonia will have been expelled when 100 c.c. of liquid has distilled. The distillate is then "nesslerised," made up to 250 c.c., and the tint compared with a standard ammonium sulphate solution containing 1 mg. of nitroger per c.c. The comparison will give the apparent nitrogen content which must be corrected by a factor (obtained from a curve giver in the original paper) in order to arrive at the actual nitroger content. This is due to the fact that intensity of colour and ammonia concentration are not directly proportional. G. F. M.

**Kjeldahlisation of Mononitrophenols, Mononitrobenzoic Acids, and Mononitrocinnamic Acids.** R. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1922, **55**, [*B*], 1380—1389).—A con tinuation of previous work (A., 1920, ii, 50), in which it was shown that the Kjeldahl-Gunning method gives accurate results only for the ortho-derivatives when applied to the mononitrophenols and mononitrobenzoic acids.

The Kjeldahlisation of mononitro-phenols and -benzoic acids by sulphuric acid without addition of potassium sulphate gives correct values for the ortho-, and low values for the meta- and para-com pounds; it is remarkable that the latter are considerably higher than those given hy the Kjeldahl-Gunning method.

Stepwise Kjeldahlisation according to Kjeldahl-Gunning shows that in the case of *o*-nitrophenol and *o*-nitrobenzoic acid, the major part of the nitrogen value is attained during the stage of the initial discoloration which occurs at the commencement of the heating

and the theoretical nitrogen value is almost attained at the period of most violent action. With *p*-nitrobenzoic acid, on the other hand, practically no nitrogen value is attained at the stage of initial darkening and the nitrogen is almost entirely present in such a form that the calculated nitrogen value is observed after addition of phenol; at the period of most violent action, the "converted" nitrogen increases somewhat, whereas that "convertible" by subsequent addition of phenol declines, ultimately becoming reduced to zero when the solution is colourless.

In the case of *p*-nitrobenzoic acid, the replacement of potassium sulphate in the Kjeldahl process by copper oxide or mercuric oxide leads to analytical results which are in harmony with the calculated values. The activity of copper oxide is not affected by the presence of potassium sulphate, whereas that of mercuric oxide is greatly depressed. The activity of sodium sulphate is inferior to that of potassium sulphate and approximately equal to that of lithium sulphate.

A further series of experiments is described in which the Kjeldahlisation of *p*- and *m*-nitrobenzoic acid and of *p*-nitrophenol is effected by the presence of potassium sulphate; the volatile products are collected and heated with concentrated sulphuric acid, phenol, and copper oxide. *p*-Nitrobenzoic acid and *p*-nitrophenol are found to behave in an entirely different manner; the former yields a volatile nitrogenous compound in which the nitrogen can be converted into ammonia by sulphuric acid, phenol, and copper oxide, whereas the latter undergoes a far more complex decomposition with the formation of products which do not yield ammonia under the described conditions.

In striking contrast to the nitrobenzoic acids, the three nitrocinnamic acids yield almost the whole of their nitrogen as ammonia when heated with sulphuric acid and potassium sulphate. Satisfactory results are also obtained with sulphuric acid alone or mixed with copper oxide. H. W.

**A Micro-method for the Estimation of Ammonia in Blood and in Organic Fluids.** K. L. GAD-ANDRESEN (*J. Biol. Chem.*, 1922, **51**, 367—372).—One c.c. of blood is used for the estimation. After addition of borate, it is evaporated to dryness by heating at 25° in a current of dry air. The ammonia thus removed is absorbed in sulphuric acid, decomposed by hypobromite, and the nitrogen measured in Krogh's microrespirometer as in the author's urea method (A., 1920, ii, 646). The method is also applicable to secretions, but not to tissues. E. S.

**New Insoluble Organic Nitrates.** JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1922, **20**, 84—92).—In a study of organic compounds giving precipitates or turbidities with nitrates, the following compounds are mentioned as new precipitants: *p*-dianisylphenetylguanidine hydrochloride (acoine),

$$OEt\cdot C_6H_4\cdot N:C(NH\cdot C_6H_4\cdot OMe)_2,HCl;$$

dicyanodiamide, $NH:C(NH_2)\cdot NH\cdot CO\cdot NH_2$, produced by the hydrolysis of dicyanodiamidine, $NH:C(NH_2)\cdot NH\cdot CN$; the hydrochloride

of *hydrocupreine ethyl ether (optoquine), hydrastine hydrochloride.* The common features in the constitution of nitrate precipitants is discussed. G. W. R.

**So-called Di-9 : 10-monohydroxyphenanthrylamine suggested as a Reagent for Nitric Acid and Phenanthroxazine.** B. Foresti (*Gazzetta*, 1922, **52**, i, 278—285).—The author has investigated Bamberger and Grob's phenanthroxazine (A., 1901, i, 280) and finds that the melting point 350—355° given by these authors is that of a mixture of the compound with its decomposition products. The value obtained for the melting point depends on the initial temperature of the heating bath. With a bath at 422° (non-corrected), fusion occurs after the lapse of six seconds from the time of immersion, and since this is the length of time required for the tube and substance to assume the temperatnre of the bath, the melting point is taken as 422°.

It is found, further, that the substance obtained by Schmidt and Lumpp (A., 1910, i, 312; ii, 450) by the action of aqueous ammonia on dihydroxyphenanthrene, and described by these authors as di-9(10)-monohydroxyphenanthrylamine, consists of a mixture of phenanthroxazine with impure phenanthrazine and that the characteristic behaviour of the substance towards nitrates is due to the presence of the phenanthroxazine. In testing for nitrate, use is made of a solution of 0·01 gram of phenanthroxazine in 100 c.c. of concentrated sulphuric acid, and as dilution of this blue solution with water may give rise to a violet coloration similar to that obtained with nitrates, the substance to be tested must not be in aqueous solution. The dry residue left in a porcelain dish by a drop of the liquid to be examined is treated with a drop of the reagent; in presence of a nitrate, a reddish-violet coloration is formed, hut if the amount of nitrate is very small, only a violet ring appears after some time. In this way $1 \times 10^{-7}$ gram of nitric acid is detectable. This reaction is not disturbed by moderately high proportions of chlorate or chromate, and although slightly less sensitive than that of brucine with nitric acid, is not given by nitrous acid. The coloration is not destroyed hy sulphur dioxide, but is changed to pale yellow by stannous chloride. T. H. P.

**Estimation of the Nitro-group in Aromatic Organic Compounds. II.** T. Callan and J. A. Russell Henderson (*J. Soc. Chem. Ind.*, 1922, **41**, 157—161T).—The low results obtained with certain compounds by the Knecht-Hibbert reduction method with titanous chloride for the estimation of nitro-groups is due in the case of readily chlorinated substances such as *o*-nitroanisole, α-nitronaphthalene, etc., to chlorination by the titanous chloride and the reducing action of the thereby liberated hydrogen, whereby a lesser amount of titanous salt is oxidised than would otherwise he the case. This source of error can be entirely obviated hy using titanous sulphate solutions instead of the chloride, or may be very largely avoided even by using sulphuric acid instead of hydrochloric acid to acidify the titanous chloride solution. In general, the greater the excess of hydrochloric acid used the greater will be

e error due to chlorination. Another source of error, due to the ·latility in steam of the simpler nitro-compounds, may be obviated sulphonating, but much more simply by reducing under a ound-in reflux condenser about 9 inches long. By adopting ese modifications and precautions, it is shown that, contrary to atements by English (A., 1920, ii, 776), nearly all types of nitro-mpounds can be accurately estimated, including mononitro-drocarbons, chloronitro-compounds, and other negatively substi-ted nitrohydrocarbons. Recrystallised *p*-nitroaniline is recom-ended as the ultimate standard for the titanous solutions.

G. F. M.

**Separation of Phosphoric Acid in Qualitative Analysis.** . BALAREFF (*Z. anorg. Chem.*, 1922, **121**, 254—256).—The pre-pitates of the ammonium sulphide group (Groups III and IV ken together) are dissolved in hydrochloric acid (solution is thus ee from cobalt and nickel) and the solution neutralised with nmonia. A large excess of lead nitrate is added and then sodium etate until the solution is neutral to methyl-orange. The phos-oric acid is precipitated as lead phosphate, mixed with lead loride and phosphates of ferric iron, chromium, and aluminium. ie large excess of lead-ion, however, ensures that some ferric, romium, and aluminium-ions remain in solution. The excess of ad is then removed by hydrochloric acid. The author claims that is method possesses advantages in speed and completeness of paration over the older methods. W. T.

***Effect of Adsorption by Stannic Sulphide on the Estimation* Phosphates.** SUETARÔ KIKUCHI (*J. Chem. Soc. Japan*, 1922, , 329—333).—When phosphate is determined by the usual ethod, it is found after the tin in solution is removed as sulphide, at there is a deficiency of phosphate. This is due to adsorption the phosphate by stannic sulphide; stannous sulphide, on the ntrary, does not adsorb phosphate; therefore the quadrivalent n in the solution is reduced to the stannous state by zinc in the esence of carbon dioxide and removed as sulphide. Estimation the phosphate in the filtrate then gives correct values. K. K.

**The Citric Solubility of Mineral Phosphates.** J. F. TOCHER . *Agric. Sci.*, 1922, **12**, 125—143).—The proportion of phosphoric id extractable by citric acid from basic slags and mineral phos-iates is closely dependent on the conditions of experiment. The ree variables being the amount of citric acid used, the amount mineral phosphate used, and the volume of liquid used, the ithor has investigated the influence on the amount of phosphoric id extracted of varying one of these factors whilst keeping the her factors in a constant ratio. With constant weights of mineral iosphate and citric acid, the amount of phosphoric acid dissolved creases with the volume. With constant weight of mineral iosphate and constant volume, the amount of phosphoric acid ssolved increases with increase of the amount of citric acid used. ith constant weight of citric acid and constant volume, the

amount of phosphoric acid extracted decreases with increase in the amount of mineral phosphate used. The quantitative relationships are connected with considerations of mass action and it is shown that the solubility curves obtained can be made to fit an empirical formula. It is held that citric solubility is influenced by so many factors that it is an untrustworthy test of the agricultural value of mineral phosphates and slags. The only standard tests to be accepted are total phosphate content, fineness of grinding, and freedom from injurious substances. G. W. R.

**Invisible " Mirrors " of Arsenic, Antimony, and Bismuth.** HERMANN SCHEUCHER (*Monatsh.*, 1921, **42**, 411—420).—Bettendorff's test for arsenic, consisting in reducing an oxide of arsenic with stannous chloride and hydrochloric acid, when arsenic is thrown down as a voluminous, brown precipitate, has been developed into an extremely sensitive microchemical test. The reactants are introduced into a capillary tube which is then sealed to a point at one end and heated for a short time in a bath of boiling amyl alcohol (130°). The tube is then centrifuged and the arsenic appears as a brown precipitate in the point of the capillary. In this way, 0·01γ of arsenic (γ=0·001 mg.) can be detected at a dilution of 1 in 250,000. By contrast, the magnesium ammonium arsenate test is uncertain with 0·1γ of arsenic. The test is not interfered with by antimony, tin, lead, copper, or cadmium. The Marsh test, using Lockemann's method (A., 1905, ii, 353), is sensitive to 0·1γ, whilst with less arsenic the mirror becomes scarcely visible, and invisible with 0·04γ. If, however, the glass capillary containing the mirror, or supposed mirror, is treated with bromine vapour to oxidise the arsenic, and the Bettendorff test is then applied as above, as little as 0·01γ of arsenic can be detected.

The Marsh test applied to antimony is sensitive to 0·2γ, but the presence of antimony in invisible mirrors can be demonstrated by the luminescence test described by Paneth (A., 1919, ii, 68). Bismuth can be detected in a similar way when the hydride is prepared by Paneth's method. The mirror is dissolved in a drop of nitric acid, which is then transferred to a piece of ignited calcium carbonate held in a platinum loop and the flame test applied. For antimony, the limit of sensitiveness is 0·001γ. An invisible mirror can also be " developed " with a solution of ferrous sulphate in acetic acid containing silver nitrate. After a short time, silver is deposited in the place where the mirror should be. The reaction is extraordinarily sensitive, but, unfortunately, a glass tube which has merely been ignited with only a current of air passing through may give the reaction, although a quartz tube will not do so.

E. H. R.

**Colorimetric Estimation of Arsenic by means of Quinine Molybdate.** D. CHOUCHAK (*Ann. Chim. analyt.*, 1922, **4**, 138—142).—A solution containing a trace of arsenic is oxidised with nitric acid, evaporated to dryness, and the residue treated with 0·5 c.c. of 17·5% nitric acid, 4·5 c.c. of water, and 20 c.c. of quinine molybdate reagent; the turbidity produced is compared with that

given by a known amount of arsenic under similar conditions. As little as 0·00002 mg. of arsenic gives a visible turbidity. The reagent is prepared by dissolving 0·5 gram of quinine hydrochloride in 10 c.c. of water, adding 5 c.c. of arsenic acid solution (containing 0·01 mg. of arsenic per c.c.), 10 c.c. of 17·5% nitric acid, and 1 c.c. of sodium molybdate solution (3·5 grams of sodium carbonate and 9·5 grams of molybdic acid per 100 c.c.); after a few minutes, the mixture is diluted with water to 120 c.c., and filtered through a filter-paper moistened previously with nitric acid and washed. If heavy metals are present in the solution under examination, the arsenic must be separated by distillation with hydrochloric acid, potassium bromide, and hydrazine sulphate, the distillate oxidised with nitric acid, evaporated to dryness, and the dry residue used for the estimation. W. P. S.

**Inadequacy of the "A.R." test for Alkalis in Calcium Carbonate.** W. SINGLETON and H. WILLIAMS (*Analyst*, 1922, **47**, 252—254).—Only about 50% of the total extractable sodium carbonate is washed out on boiling 5 grams of calcium carbonate with 50 c.c. of water for ten minutes. The alkalis present in 5 grams of "A.R." calcium carbonate were therefore determined by the Lawrence Smith method (this Journal, 1871, 442) and the amount of sodium carbonate obtained was more than ten times that given by the "A.R." method. The result was checked by decomposing 5 grams of the calcium carbonate with hydrochloric acid and precipitating the calcium twice with ammonium carbonate and ammonium oxalate. Substantially the same result was obtained. It therefore appears that only about 10% of the alkali carbonates present in the calcium carbonate are removed by one extraction with water. H. C. R.

**A Comparison of the Calcium Content of some Virgin and Cultivated Soils of Kentucky by an Improved Method for the Estimation of this Element.** O. M. SHEDD (*Kentucky Agr. Exp. Sta. Bull.*, 236 (October 1921).—In estimating the total calcium in the soils, 1 gram of soil (passing through a 100-mesh sieve) is fused with 5 grams of a mixture of sodium and potassium carbonates (10 : 13) for ten minutes. The fused mass is dissolved in hydrochloric acid, evaporated to dryness, and the silica dehydrated. The residue is extracted with dilute hydrochloric acid and the silica filtered off. Filtrate and washings should not exceed 100 c.c. The solution is made just alkaline to litmus with strong ammonia and then just acid with hydrochloric acid. The solution, which is not always perfectly clear at this stage, is heated to boiling and the calcium precipitated by adding 1—2 grams of solid ammonium oxalate. Further addition of hydrochloric acid may now be necessary to maintain the solution acid to litmus. After two to three minutes' boiling, the solution is placed on the steam-bath for a few hours and allowed to remain over-night. The precipitate is filtered, washed twice with water, and ignited to convert it into oxide or carbonate. This is redissolved in acid and manganese precipitated by the addition of bromine

and excess of ammonia. After heating until only a little ammonia remains, the solution is made faintly acid with oxalic acid and filtered. The calcium is then precipitated from the filtrate as before and finally weighed as oxide. A. G. P.

**Flame Reactions of Thallium.** JACOB PAPISH (*Proc. Indiana Acad. Sci.*, 1918, 166—169).—Thallous chloride dissociates in a Bunsen flame to the free metal which colours the flame and may be precipitated on a cold surface as a brown mirror. In a hydrogen flame in air, thallous chloride produces five zones of luminescence. Metallic thallium will condense from the innermost cone on a cold snrface but not from the outer cone where the luminescence is probably due to oxidation of the thallium.

CHEMICAL ABSTRACTS.

**Tervalent Titanium. II. Estimation of Copper and Iron in the Presence of each other.** WILLIAM M. THORNTON, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 998—1001; cf. A., 1921, ii, 279).—A method is described for the estimation of iron and copper in the presence of one another by means of a standard solution of titanium trisulphate. The method is as follows. The mixture of cupric and ferric sulphates is dissolved in less than 100 c.c. of water, acidified with 10 c.c. of 1 : 1-sulphuric acid, and cooled to 15°. A quantity of 10% ammonium thiocyanate solution from 2·5 to 5 c.c., depending on the amount of copper anticipated, is added and the solution titrated with a standard solution of titanium trisnlphate until the pink colour just vanishes. The titre gives the sum of the copper and iron present. The whole is then heated to incipient ebullition, to coagulate the cuprous thiocyanate, cooled, and filtered. The precipitate is thoroughly washed with cold water and the filtrate and washings are cooled to 15°. The solution has by this time probably become pink again, due to oxidation by air. If so, the colour is bleached by the careful addition of titanium trisulphate, and sufficient silver nitrate (2·5—5 c.c. of 25% solution) is added to precipitate the whole of the thiocyanate. The ferrous iron is then titrated with a standard solution of potassium permanganate. The method is shown to be accurate and trustworthy, but the precaution of previously testing the titanium solution for iron must be taken, and if such is found the permanganate value corrected for this amount. J. F. S.

**Quantitative Analysis of Aluminium Alloys, especially of Duralumin.** E. MENDES DA COSTA-VET (*Chem. Weekblad*, 1922, **19**, 249—251).—The alloy of aluminium introduced for airships by the Dürener Metallwerke contains Cu 3·5—4·5%, Mn 0·5—1·0%, Mg 0·5%. The methods of Collit and Regan (A., 1918, ii, 175) and of Withey (A., 1916, ii, 538) for analysis of this alloy are unsatisfactory, since in the first the magnesium is almost completely carried down in the ammonia precipitation of iron, manganese, and aluminium, whilst in the second it is impossible to precipitate the magnesium from the tartaric acid solution by means of pyrophosphate.

It was found that magnesium can best be estimated after removal of copper by means of hydrogen sulphide, and of iron, aluminium, and part of the manganese by means of ammonium chloride and ammonia, the latter separation being performed twice, by precipitation with phosphate. Some of the manganese remains from the ammonia precipitation, and is weighed with the magnesium as pyrophosphate; this is estimated by redissolving the precipitate and titrating with permanganate.

The ammonia precipitation must be carefully carried out, and the liquid filtered immediately to avoid separation of magnesium at this stage. S. I. L.

**The Quantitative Estimation and Separation of Aluminium.** GERHART JANDER and ERWIN WENDEHORST (*Z. angew. Chem.*, 1922, **35**, 244—247).—Precipitation of large amounts of aluminium hydroxide from solutions containing other metals such as magnesium and manganese leads to such high results that the direct estimation of aluminium in alloys consisting chiefly of aluminium is not possible by the usual methods. In such cases, the authors recommend heating the alloy in a current of well-dried hydrogen chloride at 200°, whereby all the aluminium sublimes as chloride together with small amounts of silicon, magnesium, and manganese chlorides, whilst iron, copper, and zinc remain in the boat. The sublimate is dissolved in dilute nitric acid and the solution evaporated repeatedly with further quantities of the same acid until all chlorine is expelled. The silica that separates is removed by filtration and the solution is evaporated to dryness. The residue is ignited, gently at first, then strongly, and weighed as aluminium oxide containing some manganese and magnesium oxides, which are determined separately, the former colorimetrically and the latter as pyrophosphate, and deducted. [Cf. *J. Soc. Chem. Ind.*, 1922, July.] A. R. P.

**A Proposed Estimation of Chromium and Nickel in Steel.** FRITZ SIMION (*Chem. Ztg.*, 1922, **46**, 504).—The sample is dissolved in aqua regia, the solution neutralised and poured into an excess of a solution of sodium hydroxide containing hydrogen or sodium peroxide. After boiling to expel oxygen, the precipitate is collected on a Nutsche filter, well washed, then returned to the beaker and digested with ammonia and ammonium carbonate to extract the nickel. The chromate in the filtrate is estimated by any suitable method. [Cf. *J. Soc. Chem. Ind.*, 1922, July.] A. R. P.

**Applications of Amalgams in Volumetric Analyses. IV. The Uses of Cadmium Amalgam.** NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 333—340).—In earlier papers (A., 1921, ii, 596, 714), the volumetric estimation of molybdenum, titanium, etc., after reduction by means of liquid zinc amalgam was described. To extend the method, the zinc is now replaced by cadmium. The method of preparation of the amalgam and the reducing operation are practically the same as in the former case. In the cases of molybdenum and iron, the cadmium amalgam acts

as well as the zinc amalgam, but in the cases of vanadium and titanium, the reduction is not complete. With uranium, it is necessary to carry out the reduction in an atmosphere of carbon dioxide. K. K.

**The Estimation of Uranium in Presence of Phosphoric Acid.** A. SCHOEP and W. STEINKUHLER (*Bull. Soc. chim. Belg.*, 1922, **31**, 156—159).—The analysis of dewindtite (this vol., ii, 305) and of stasite (this vol., ii, 386), phosphates of uranium, and lead, necessitated more satisfactory methods than those hitherto used. The following procedure has given trustworthy results for both phosphate and uranium in a series of control experiments. Silica and elements which are precipitated by hydrogen sulphide in acid solution are first eliminated, the uranium is oxidised by means of nitric acid, and the phosphoric acid then precipitated with molybdate solution. Addition of ammonia transforms the uranium into ammonium uranate; from this the metal is precipitated as uranium sulphide on the addition of ammonium sulphide, the precipitate being washed until the washings are free from molybdenum. No solution and reprecipitation is necessary. H. J. E.

**Iodometric Studies. II.** BOHDAN KÖHLER (*Chem. Listy*, **16**, 87—91; cf. A., 1921, ii, 410).—The best results in the iodometric titration of tin are obtained by dissolving the tin in $6N$-hydrochloric acid, adding to this a known amount of iodine dissolved in potassium thiocyanate, and determining the excess of iodine with a standardised sodium thiosulphate solution.

Contrary to the observation of Zulkowski and Bruhns (*J. pr. Chem.*, 1859, **103**, 351), the velocity of the reaction $Cr_2O_7'' + 14H^{\cdot} + 6I' \longrightarrow 2Cr^{\cdot\cdot\cdot} + 7H_2O + 6I$ is quite considerable.

The titration of tin by means of potassium dichromate solution gives exact results if atmospheric oxygen is excluded from the solutions. Since it is, in practice, difficult to have air-free solutions of potassium dichromate, a correction of +0·068 mg. of tin per c.c. of aqueous aerated potassium dichromate solution is advocated. This correction is based on the assumption that the solubility of oxygen in decinormal potassium dichromate solution is little different to that in pure water. R. T.

**Reduction of Vanadic Acid Solutions with Mercury.** LE ROY W. MCCAY and WILLIAM T. ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1018—1021; cf. this vol., ii, 217).—When vanadic acid in the presence of sulphuric or hydrochloric acid is vigorously shaken with mercury the vanadium is reduced to the quadrivalent state according to the equation $2HVO_3 + 2Hg + 3H_2SO_4 = 2VOSO_4 + Hg_2SO_4 + 4H_2O$. If the solution before shaking is mixed with a little more sodium chloride than is equivalent to the mercurous sulphate formed, the whole of the mercury is precipitated as mercurous chloride and a pure blue solution left which may be quantitatively titrated with potassium permanganate when the reaction

epresented by the equation $10VOSO_4+2KMnO_4+12H_2O=$ $0HVO_3+K_2SO_4+2MnSO_4+7H_2SO_4$ takes place. A method of stimating vanadic acid by means of the above reactions is described. The solution of vanadic acid containing sulphuric acid and the equisite amount of sodium chloride (0·3 gram for each 50 c.c. f $N$/10-permanganate required) is diluted to 100 c.c., placed in a toppered bottle, and vigorously shaken with 20 c.c. of mercury or five minutes. The liquid above the grey mercury mixture is lecanted into a small beaker and poured through a suction filter. The residue in the bottle is washed four times by decantation, 0 c.c. of water being used for each washing, and the washings are everally decanted into the beaker and then through the filter. The total filtrate is diluted to 250 c.c., heated at 80—90°, and itrated with permanganate to the faintest pink. The whole rocess may be completed in thirty minutes; it gives results which re identical with those obtained by the sulphur dioxide method, nd since uranic acid and arsenic acid are not reduced by mercury, he method may be employed in the presence of these acids.

J. F. S.

**Detection of Antimony in Analysis.** TH. SABALITSCHKA nd H. SCHMIDT (*Ber. deut. Pharm. Ges.*, 1922, **32**, 132—135).—To obviate the necessity of using platinum foil, antimony may e detected in the solution of the sulphides of antimony and tin n concentrated hydrochloric acid as ordinarily obtained in the ourse of analysis, by diluting a portion of this solution with an qual volume of water, adding a piece of arsenic-free zinc to the ooled liquid in a test-tube, and allowing the issuing gases to mpinge on a piece of filter-paper freshly moistened with a 10% olution of silver nitrate. In presence of antimony the paper vill become quite black on the under side within two minutes, r immediately if considerable quantities are present. A slight rown coloration is to be disregarded, and it is important that the ilver solution is not too concentrated, otherwise small amounts of ydrogen antimonide may cause only a brownish-yellow coloration nstead of black, as is always obtained with dilute silver solutions.

G. F. M.

**Detection of Benzene in Light Petroleum.** P. SCHWARZ Chem. Ztg., 1922, **46**, 401).—If 5 c.c. of pure light petroleum are dded to 2 c.c. of a mixture consisting of equal volumes of aniline nd 95% alcohol, the aniline separates as a layer; should as little s 5% of benzene be present in the light petroleum, the aniline loes not separate from the mixture and a clear solution is obtained. f desired, the light petroleum may be fractionated previously, nd the test applied to the fraction having b. p. 80° to 110°.

W. P. S.

**The Detection and Estimation of Acidity and Alkalinity n Cotton Fabrics.** HUBERT FRANK COWARD and GLADYS MARY WIGLEY (*Trans. Text. Inst.*, 1922, **13**, 121—126).—The esting of cotton fabrics for traces of strong acids, such as might

give rise to "tendering," is complicated on the one hand by the fact that cotton exhibits a preferential attraction for the basic constituent of neutral salts and thus produces an acid reaction in their aqueous solutions, and, on the other, by the fact that cotton retains absorbed mineral acids so tenaciously that they can only be completely removed by repeated extractions with boiling water. It is now shown that the first factor is of far less moment in the titration of acid in the presence of the fabric than the second factor would be in a titration of the extract. Acidimetry of bleached cloth, correct to 0·01% of hydrochloric or sulphuric acid, and alkalimetry, correct to 0·02% of soda, calculated as sodium hydroxide, can be carried out by titrations with 0·02*N*-solutions, at the boil, in the presence of the fabric, using phenolphthalein as indicator. A fabric which contains up to 0·1% of sulphuric acid might, however, retain up to 0·05% after two extractions with boiling water.

The use of organic indicators, and a mixture of potassium iodide, iodate, and starch, for "spot" tests on the fabric is also described, and the sensitivity limits are indicated. Methyl-red is responsive to about 0·005% of strong acid or alkali. Difficulties arising from the presence of weak acids, soap, "finishing" compositions, and dyes are briefly discussed, but methods for testing raw cotton fabrics have still to be investigated. J. C. W.

**Estimation of Volatile Fatty Acids.** G. WIEGNER and J. MAGASANIK (*Mitt. Geb. Lebensmitt. Hyg.*, 1919, **10**, 156—174; from *Bied. Zentr.*, 1922, **51**, 140—145).—In the distillation of aqueous solutions of volatile fatty acids the following relationship is established, $(\log y_1 - \log y_2)/(\log x_1 - \log x_2) = $ constant, where $y_1$, $y_2$, are the amonnts of acid in terms of c.c. of standard alkali required for neutralisation of the residue at the beginning and end of a distillation interval and $x_1$, $x_2$, the corresponding amounts of water. Values of the constant are given for the volatile fatty acids. The formula is applied to the estimation of volatile acids in silage. An example is given in which an aqueous extract containing acetic and butyric acids is made up to a known volume and distilled to half volume, the operation being repeated three times. From the titre of the distillates the acid value of each successive residue is obtained, whence by calculation the amounts of acetic and butyric acids respectively in the original extract are obtained. The method may be applied to the estimation of volatile acids in wines. Analytical figures are given for the amounts of acetic, butyric, and lactic acids in different kinds of silage. G. W. R.

**Analysis of Acetic Anhydride.** A. RECLAIRE (*Perf. Essent. Oil Rec.*, 1922, **13**, 148—149).—Ten grams of acetic anhydride are weighed out into a 250 c.c. flask, diluted with 75 c.c. of water free from carbon dioxide, and heated on a water-bath for fifteen minutes under a reflux condenser. The product is diluted to 500 c.c. with a further quantity of carbon dioxide-free water, and 50 c.c. are titrated with *N*/2-potassium hydroxide solution free from carbonate. The percentage of acetic anhydride present is then (c.c. *N*/2 KOH used ×17·144)—570·45. The necessity for using

vater and alkali free from carbon dioxide is emphasised. The atter is readily obtained by mixing 1000 c.c. of ordinary potassium ıydroxide solution with 50 c.c. of milk of lime, and after keeping ıne or more days the clear liquid is syphoned off and standardised.
G. F. M.

**Detection and Estimation of Free Sulphuric Acid and Sulphoacetates in Cellulose Acetates.** M. ENTAT and E. VULQUIN (*Ann. Chim. analyt.*, 1922, **4**, 131—135).—To estimate ree sulphuric acid, 10 grams of the cellulose acetate are digested or thirty minutes with 200 c.c. of water at 15°, the mixture is hen filtered, and the filtrate is titrated with standardised barium ıydroxide solution, the end-point being determined electrometrically. There is a sharp break in the titration curve when all the free sulphuric acid has been neutralised. None of the samples examined by the authors contained free sulphuric acid, and it is suggested hat this acid is not present in normal cellulose acetates, the quantities found by other observers being actually due to the presence of alkali or alkaline-earth sulphates, acetic acid giving the acid reaction. Cellulose acetate prepared by methods involving the use of sulphuric acid as catalyst invariably contains sulphoacetic acid combined with the cellulose ester. The sulphoacetate is estimated by heating 10 grams of the cellulose acetate with 50 c.c. of water in an autoclave at 125° for five hours; the sulphuric acid resulting from this hydrolysis is then titrated electrometrically. The amount of sulphuric acid present as sulphoacetate in well-prepared cellulose acetate is always less than 0·03%. W. P. S.

**Determination of the Iodine Value of Aliphatic and Aromatic Unsaturated Compounds.** D. HOLDE, P. WERNER, IDA TACKE, and C. WILKE (*Chem. Umschau*, 1922, **29**, 185—188).—The determination of the iodine value is a valuable criterion of the purity of higher unsaturated fatty acids and their derivatives when other methods, such as molecular weight and melting point determinations, fail, and has been used by Holde and Wilke in the case of erucic acid (this vol., i, 317). For this purpose, the Hanus reagent (10 grams of iodine monobromide in 500 c.c. of glacial acetic acid) is preferred, as it gives results in close agreement with those obtained with Hübl's reagent, and is more easily prepared, more stable, and more rapid in action, fifteen minutes being sufficient, with about 50% excess of the reagent, for the completion of the reaction. Accurate results are also obtained with aromatic unsaturated compounds, for example, safrole, under similar conditions. Nevertheless, as is well known, anomalous results are given by the Hübl-Waller reagent, and by Wijs's reagent for cholesterol and phytosterol, the former giving abnormally low, and the latter abnormally high results. With the original Hübl solution, however, consistent, although slightly high results (73—77 compared with 65·7 theoretical) were obtained with cholesterol, but with phytosterol values varying from 41 to 76 were obtained, according to the duration of the reaction and the excess of Hübl solution employed. With both alcohols, Wijs's solution gave values of

about 135, that is, approximately double the theoretical. similar difference in the results obtained with the Hübl-Waller with Wijs's reagents has been observed with mineral lubrica oils and with naphthenic acids, which may indicate the pres of cholesterol derivatives in these products. G. F. M

**Estimation of the Various Acids of Wine.** TH. VON FELL BERG (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 217—255).—The aut has developed a scheme of analysis by means of which the sepa proportions of weak organic acids (tannic acids) and of tart malic, succinic, and lactic acids may be estimated. [Cf. *J. Chem. Ind.*, 1922, 514A.] T. H. ]

**A Colorimetric Method for the Estimation of Homogent Acid in Urine.** A. P. BRIGGS (*J. Biol. Chem.*, 1922, **51**, 4 454).—The method depends on the reduction of phosphomoly acid by homogentisic acid (cf. Bell and Doisy, A., 1920, ii, 7 The diluted urine is treated first with a solution containing 5% ammonium molybdate in 5*N*-sulphuric acid and then with a solution of potassium dihydrogen phosphate. The colour duced is compared with a quinol standard, experiments ha shown that 1 mg. of quinol is equivalent to 0·79 mg. of ho gentisic acid. Albumin and sulphides interfere with the react but these may be removed, if present, by means of trichloroac acid and silver sulphate. E.

**Estimation of the Iodine–Bromine Number without us Potassium Iodide.** L. W. WINKLER (*Z. Unters. Nahr. Genus* 1922, **43**, 201—204).—The use of potassium iodide in this es ation can be avoided by treating the oil or fat with exces bromine, adding a solution of arsenious oxide, and titrating excess of the latter with potassium bromate solution. A bl estimation is carried out, using the same quantities of the reag as for the actual estimation and allowing them to react for same length of time. The results are almost identical with t obtained from using potassium iodide solution according to original method (*ibid.*, 1916, **32**, 358). H. C. I

**Use of Semi-microchemical and Microchemical Meth in Place of Macrochemical Methods in the Analysis of Foo** H. LÜHRIG (*Pharm. Zentr.-h.*, 1922, **63**, 218—221, 227—232 The Reichert-Meissl, Polenske, saponification, and iodine num of fats and oils may be estimated on quantities of substance var from 0·02 to 0·2 gram. The procedure employed is similar to used in the methods in their usual form and is described in de in the case of the Reichert-Meissl number, the distillation requ about five minutes, 10 c.c. of distillate are collected (when gram of fat is taken), and the result obtained must be multip by 0·9 to obtain the true Reichert-Meissl number. W. P.

**The Constants of Indian Beeswax.** O. D. ROBERTS H. T. ISLIP (*Analyst*, 1922, **47**, 246—251).—Tables are give the constants of twenty-three samples of honeycomb and

collected under the supervision of District Officers in Bengal, Eastern Bengal, and Assam. The low acid values obtained are remarkable, being in many cases lower than 6, the figure hitherto accepted as the lowest representing unadulterated Indian beeswax. Both Weinwurm's test and Salamon and Seaber's test are shown to be untrustworthy. H. C. R.

**The Estimation of Aldehydes and Ketones by means of Hydroxylamine.** A. H. BENNETT and F. K. DONOVAN (*Analyst*, 1922, **47**, 146).—The method originally proposed for the estimation of citral in lemon oil (A., 1909, ii, 192) can be applied to other aldehydes and ketones. With formaldehyde, acetone, and benzaldehyde, very close results are obtained. Carvone requires rather more carefully standardised conditions. The analyses of citronellal and citral are slightly less accurate. No satisfactory results could be obtained for camphor. The hydroxylamine hydrochloride used for this process should be recrystallised from water, and not from alcohol. A. G. P.

**The System Camphor–Alcohol–Water in Relation to the Titration of Camphor-spirit.** K. SCHERINGA (*Pharm. Weekblad*, 1922, **59**, 389—395).—The proportions of camphor, alcohol, and water which can remain in equilibrium in a single-phase system at various temperatures have been determined, and the results expressed graphically on the ordinary equilateral triangle presentation. Known solutions of alcohol and camphor were treated with water until a permanent separation occurred, and the increase in weight was then determined.

It is shown that many mixtures can be prepared to satisfy the requirements laid down in the Pharmacopœia, and that in analysing the preparation as recommended by titration with water the temperature must be kept between 20° and 25°, and also that the amount of camphor which can be added and held in solution at 15° should be specified. S. I. L.

**The Detection of Vernin.** H. STEUDEL and R. FREISE (*Z. physiol. Chem.*, 1922, **120**, 126—129).—Vernin when boiled with acetic anhydride containing a small particle of sodium acetate and then cooled yields lustrous, pale rose needles, which after twice recrystallising from absolute alcohol give colourless prismatic needles of triacetylvernin, m. p. 226°, $[\alpha]_D^{15}$ +2·306°. S. S. Z.

**The "Cotton Wool Plug" Test for Indole.** S. N. GORE (*Indian J. Med. Research*, 1921, **8**, 505—507).—The under-surface of the plug is evenly moistened, first with a few drops of a solution of 1 gram of *p*-dimethylaminobenzaldehyde in 95 c.c. of absolute ethyl alcohol and 20 c.c. of hydrochloric acid, and then with a few drops of a solution of 1 gram of potassium persulphate in 100 c.c. of distilled water. The tube containing the plug, pushed down to about an inch above the surface of the broth culture, is placed upright in a gently boiling water-bath and heated for about fifteen minutes. Indole, when present to so small an extent as

0·0005 mg. per c.c. of the broth culture, volatilises and develop on the plug a rose colour which is viewed through the tube.

CHEMICAL ABSTRACTS.

**The Detection and Estimation of Monoamino-acids.** R ENGELAND (*Z. physiol. Chem.*, 1922, **120**, 130—140).—The author estimated proline by means of his betaine method in glutin and elastin. The former protein showed a content of 10·9% and the latter of 4·3% of proline. The same method was applied in the case of ascitic fluid. Six and a half litres of fluid yielded 0·06 gram of the chloroaurate of the betaine of leucine and 0·025 gram. of the chloroaurate of the betaine of lysine by this method. S. S. Z.

**Colorimetric Estimation of the Amino-acid Nitrogen in Normal Urine.** OTTO FOLIN (*J. Biol. Chem.*, 1922, **51**, 393—394).—Ammonia is removed by shaking with permutite and the estimation is then carried out as for blood (cf. this vol., ii, 540).

E. S.

**The Manipulations Preparatory to the Estimation of Amino-acids in Blood.** FERNAND PETITJEAN (*Bull. Soc. Chim Biol.*, 1922, **4**, 108—114).—For the preparation of blood for the estimation of its amino-acid content by Van Slyke's method, the author recommends, from the numerous methods which have been proposed, decomposition of urea by means of the soja bean, followed by precipitation of proteins by the addition of trichloroacetic acid. Details of the technique used are given in the original.

E. S.

**Estimation of Urea from the Carbon Dioxide Produced by Urease.** ZOLTÁN ASZÓDI (*Biochem. Z.*, 1922, **128**, 391—395; cf. A., 1920, ii, 519).—An improvement in Partos's apparatus is described and examples given of its use. H. K.

**A Micro-urease Method for the Estimation of Urea in Blood, Secretions, and Tissues.** K. L. GAD-ANDRESEN (*J. Biol. Chem.*, 1922, **51**, 373—376).—The urea is first decomposed by means of urease and the ammonia then estimated by the method described for ammonia (this vol., ii, 523). A correction is made for the ammonia originally present. E. S.

**The Estimation of Guanidine.** A. H. DODD (*J. Soc. Chem. Ind.*, 1922, **41**, 145—147T).—The presence of guanylcarbamide, which is likely when guanidine has been prepared from dicyanodiamide and dilute acids, interferes with the estimation of guanidine as picrate, as this substance also gives an insoluble picrate with picric acid or ammonium picrate. It is found, however, that guanylcarbamide picrate is much more soluble in sodium hydroxide solution than the guanidine compound, and by choosing suitable concentrations it is possible to precipitate the latter whilst the former is retained in solution. The gnanidine solution, of less than 1% strength, is added to 50 c.c. of the precipitant consisting of a solution of 20 grams of picric acid in 100 c.c. of $N$/1-sodium hydroxide solution. The precipitation is carried out in hot solutions

)°), and the mixture kept for at least six hours before filtering rough a Gooch crucible. The correction which would have to applied to the weight of picrate obtained on account of its slight lubility in water can only be determined for each individual case, t empirically it was found that under the conditions above entioned washing the precipitate with only 50 c.c. of water left st about sufficient sodium picrate behind to compensate for the lubility of guanidine picrate. It was found incidentally that ecipitation of guanylcarbamide by neutral sodium picrate was a stinct improvement on the use of picric acid. G. F. M.

**The Method of Estimating Allylthiocarbimide in Mustard our.** E. LUCE and A. DOUCET (*J. Pharm. Chim.*, 1922, **25**, 458—4).—In estimating allylthiocarbimide by Dieterich's method, using nmoniacal silver nitrate, exact results may be obtained either lumetrically or gravimetrically, providing certain precautions e observed. In the case of mustard flour, the reaction is comete after six hours' contact even in the cold. Rise in temperature d extension of the time of maceration are both followed by a condary reaction which destroys some of the essence formed at st, and hence a low figure is obtained. During the first hour of aceration, this secondary reaction is negligible whatever the temrature may be. Hence to obtain accurate results the duration the maceration should be reduced to one hour and the essence t in contact with the ammoniacal silver nitrate in the cold for : hours or at 80—85° for one hour, using a flask with a reflux ndenser. W. G.

**Characteristics of Identity of a Water Distilled from the herry Laurel** HENRI PECKER (*J. Pharm. Chim.*, 1922, [vii], **25**, 4—429).—The distillate from the cherry laurel as officially epared and containing 1 gram of hydrocyanic acid per litre ould also contain a marked amount of benzaldehyde, usually ove 3 grams per litre. Under such conditions, the amount of e hydrocyanic acid does not exceed 0·25 gram per litre. The stillate should give an almost immediate precipitate, in the cold, th Denner's phenylhydrazine reagent, and with a solution of nmonium molybdate in sulphuric acid should give a deep blue lour. W. G.

**Potentiometric Titrations of and by means of Potassium errocyanide. I. The Titration of Potassium Ferrocyanide means of Potassium Permanganate.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 343—352; cf. Kelley and Bohn, A., 20, ii, 134).—In the potentiometric titration of ferrocyanides means of potassium permanganate, the former solution should ntain sufficient acid to prevent the precipitation of potassium anganese ferrocyanide, $K_2MnFeCy_6$. The acid may be either drochloric or sulphuric, the change of potential denoting the d-point being smaller with the former, but constant potential is ore rapidly attained than with sulphuric acid. The author's periments fail to confirm the objection that an error is intro-

*duced owing to the liberation of chlorine by the action of hydrochloric acid on the permanganate.* The method is accurate with ferrocyanide solutions of very small concentration. It is advantageous to add a definite quantity of potassium ferricyanide before titration, as, by this means, atmospheric oxidation of the ferrocyanide is avoided. The necessary stirring is effected by passing a current of carbon dioxide through the mixture. Details of experimental results with ferrocyanide solutions of different concentrations and in the presence of different amounts of both acids are given. H. J. E.

**The Estimation of Uric Acid in Tissue Extracts.** H. STEUDEL and K. SUZUKI (*Z. physiol. Chem.*, 1922, **119**, 166—171).—The fresh spleen from cattle contains substances other than uric acid which reduce phosphotungstic acid to blue compounds. It is therefore pointed out that in order to obtain trustworthy results with Folin's method for the estimation of uric acid in tissues it is necessary to isolate the uric acid quantitatively previously to estimating it colorimetrically. S. S. Z.

**Methods for the Estimation of the Alkaloids.** PAUL HERZIG (*Arch. Pharm.*, 1922, **259**, 249—308).—A comprehensive and critical survey of all the known methods, gravimetric, volumetric, colorimetric, refractometric, and polarimetric, for the estimation of alkaloids. Direct weighing, although possessing many obvious advantages, has the great disadvantage that it is difficult without loss to isolate the alkaloid in a sufficiently pure condition. Of all the methods suggested for weighing as insoluble salts or double salts only precipitation by picric acid, phospho- or silico-tungstic acid, or picrolonic acid (dinitrophenylmethylpyrazolone) have any practical value, and of these only the latter is considered really useful for practical purposes, and even here comparative estimations made on nux vomica seeds and extracts showed that the results obtained were always 2·5—5% low. Of the volumetric methods titration with standard acid is the most generally employed, iodometric estimations are not to be recommended, but iodometric estimation with iodide–iodate of the excess of acid unneutralised by the alkaloid gives good results except in the case of feebly basic alkaloids the sulphates of which are much dissociated, for example, narcotine, pilocarpine, and purine derivatives, and is particularly useful if much colouring matter is present. Volumetric precipitation methods using Meyer's reagent, phosphomolybdic acid, potassium ferrocyanide, or picric acid are regarded as inexact except in special cases such as ferrocyanide for the estimation of strychnine in presence of brucine, and picric acid for the cinchona alkaloids. Quantitative colorimetric and optical methods all demand the isolation of the alkaloid in a colourless condition, and they are often cumbersome as well, and consequently are very little used. G. F. M.

**The Titration of the Cinchona Alkaloids and their Salts.** N. SCHOORL (*Rec. trav. chim.*, 1922, **41**, 228—235; *Pharm. Weekblad*, 1922, **59**, 369—374).—The neutralisation curves of quinine

and hydrochloric acid have been determined, using methyl-orange, methyl-red, neutral-red and phenolphthalein as indicators, both in aqueous solution and in 50% alcohol. The addition of alcohol to the aqueous solution diminishes the dissociation constant of quinine, thus rendering the base less alkaline and increasing the hydrolysis of the salts; but as the dissociation constant of the indicators is diminished at the same time, the experimental results obtained in alcoholic solution may appear to contradict this statement. Methyl-orange and methyl-yellow are unsuitable owing to indefinite end-points. Titration of quinine as a monacid base can be carried out very accurately with the use of methyl-red. The monohydrochloride is alkaline to methyl-red and acid to neutral-red; this property may be made use of, not only for quinine, but also in the case of the other cinchona alkaloids. Cinchonine gives similar results. Experimental details of the titrations are given. H. J. E.

**[Detection of] Quinotoxine in Quinine Salts.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1922, **61**, 193—199).—The presence of quinotoxine in a salt of quinine may be detected as follows: The salt is dissolved in water, if necessary with addition of sulphuric acid, and the solution rendered alkaline by means of sodium hydroxide and extracted with ether or chloroform. After separation of the solution and evaporation of the solvent, part of the residue is carefully evaporated to dryness with a few drops of concentrated nitric acid. If quinotoxine is present, the residue thus obtained is deep yellow and is turned intense brownish-yellow by ammonia solution. The remainder of the residue from the solvent is dissolved in a little warm water acidified with acetic acid and the solution filtered if necessary. One portion is shaken with a little sodium nitrite, the nitrous acid liberated converting the quinotoxine into its nitroso- and nitroso-oximino-derivatives, which form a yellow precipitate; on quinine, nitrous acid has no action. Another portion is shaken with a drop of phenylhydrazine, the quinotoxine phenylhydrazone formed being gradually deposited as a precipitate which ultimately becomes deep orange-yellow; here also quinine remains unaffected. Bromophenylhydrazine gives a deep red coloration with quinotoxine. Solutions of quinine salts which turn yellow when sterilised probably contain quinotoxine and should not be employed for medicinal purposes. T. H. P.

**Colorimetric Methods for the Separate Estimation of Tyrosine, Tryptophan, and Cystine in Proteins.** OTTO FOLIN and JOSEPH M. LOONEY (*J. Biol. Chem.*, 1922, **51**, 421—434).—Certain defects in the method of Folin and Denis (A., 1912, ii, 1012) for the estimation of tyrosine are remedied, and an extension is made to include the separate estimation of tryptophan and cystine. When tryptophan is to be estimated, the protein is hydrolysed by means of barium hydroxide to avoid loss due to humin formation. In the case of cystine, which is decomposed by boiling alkali hydroxides, acid-hydrolysis is used. For the estimation of tyrosine and tryptophan, the hydrolysate, which must contain between 3·5% and

7·5% of sulphuric acid, is filtered from barium sulphate, and trypt- phan is precipitated from an aliquot part of the filtrate by tl addition of Hopkins and Cole's mercuric sulphate reagent. Aft separation by centrifuging, tyrosine is estimated colorimetrically i the supernatant liquid by means of Folin and Denis's phen reagent in the presence of sodium carbonate and sodium cyanid The estimation of tryptophan is made similarly in the solutic obtained by dissolving the mercuric sulphate precipitate in sodiu cyanide. In the case of cystine, sodium carbonate is added to tl hydrolysate and the cystine is reduced by means of sodium sulphit The colour produced on addition of the uric acid reagent is th compared with a standard. Results of the application of tl method to a number of proteins are given. E. S.

**A System of Blood Analysis. Suppl. III. A New Color metric Method for the Estimation of the Amino-acid Nitroge in Blood.** OTTO FOLIN [with HSIEN WU] (*J. Biol. Chem.*, 192 **51**, 377—391; cf. A., 1919, ii, 308; A., 1920, ii, 337).—The methc described is applicable to the tungstic acid filtrate and depends c the red coloration which is produced when amino-acids react wit β-naphthaquinonesulphonic acid in alkaline solution. Five or 10 c. of the filtrate are used. One per cent. sodium carbonate and 0·5% solution of the sodium salt of the sulphonic acid are adde under specified conditions and the mixture is left for thirty hou in the dark. The colour is then intensified by the addition of a acetic acid–sodium acetate solution, after which the surplus quinor is decolorised by means of a 4% solution of sodium thiosulphat A glycine solution is used as a standard. In the cases of histidi and tryptophan only one nitrogen atom reacts. Proline, trypt phan, arginine, and, to a lesser extent, alanine give unsatisfactor results. Ammonia also gives the coloration with the reagent, bu this may be neglected in blood analysis. The blue colour whic indole gives with β-naphthaquinonesulphonic acid is not produce under the conditions of alkalinity used in the estimation. E. S.

**Use of the Conventional Carbon Factor in Estimating So Organic Matter.** J. W. READ and R. H. RIDGELL (*Soil Sci* 1922, **13**, 1—6).—In soil analysis it is usually assumed that 58% of carbon represents 100% of organic substance, this ratio bein based on the results obtained by various observers. Estimatio of the carbon content of thirty-seven surface soils from differe parts of the United States showed that the percentage varied fro 30·20 to 56·27, the average being 49·26, which is about 9% belo the accepted value. The authors consider that the trustworthine of any carbon factor is doubtful; if one is employed, more accura results will be obtained if it is based on 50 to 52% of carbon.

W. P. S.

# General and Physical Chemistry.

**Optical Properties of certain Substances important in Microchemistry.** LUIGI RAITERI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 112—116).—The following refractive indices have been measured: sodium uranylacetate, 1·5082 ($\lambda$=535), 1·5044 (589), 1·5003 (671); sodium silicofluoride, 1·3112 (677), 1·3125 (589), 1·3132 (535), 1·3146 (458); potassium silicofluoride, 1·339; potassium platinichloride, 1·8103 (677), 1·8209 (606), 1·8353 (535), 1·856 (458).

T. H. P.

**Aspects of the Neon Spectrum.** LAURENCE ST. C. BROUGHALL (*Phil. Mag.*, 1922, [vi], **44**, 204—214; cf. this vol., ii, 213).—An attempt to explain the spectrum of neon by the application of the principles of Bohr and by the employment of the Langmuir hypothesis of the cubic atom. After making certain assumptions with regard to the axes of revolution of the outer electrons and taking the value $2c=1·30\times10^{-8}$ cm. for the radius of the neon atom (W. L. Bragg, A., 1920, ii, 537), it is shown that the radius of the orbit of the two inner electrons in the normal atom is $r=6·19\times10^{-9}$ cm. This figure does not apply to the atom in the gaseous state. From these two values of $c$ and $r$ the wave-lengths of the spectral lines have been calculated. The discussion of the ionised atom is very complex, the general mathematical treatment being impossible without further experimental evidence. Ionisation may occur by an electron penetrating the nucleus of the neon atom. The result of the alteration in the charge on the nucleus is to increase the number of lines in the part of the spectrum of greater wave-length.

W. E. G.

**The Structure of the Line $\lambda$=6708 Å. of the Isotopes of Lithium.** J. C. MCLENNAN and D. S. AINSLIE (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 342—348).—When strong arcs are maintained in the vapour of metallic lithium the wave-length $\lambda$=6708 Å. consisted of a close quartet with separations of 0·128 Å., 0·173 Å., and 0·165 Å. It is possible that these lines are two doublets of $Li^6$ and $Li^7$. The doublet of $Li^7$ should be about sixteen times as intense as that of the $Li^6$ form. If $a$ and $c$ of the four components is ascribed to $Li^6$ and the components $b$ and $d$ to $Li^7$, then the relative intensities would fit the relative amounts of isotopes present. On this basis, the doublet separation of $Li^6$ would be 0·301 Å. and for $Li^7$ 0·338 Å., instead of 0·55 Å. calculated on the basis of the law known to hold for the other alkali elements. The isotope separation on this view would be 0·128 Å. to 0·165 Å. If $a$ and $b$ and $c$ and $d$ are the two doublets, the average isotope separation would be 0·32 Å. Line $\lambda$=6103·77 Å. consisted of at least three well-defined components and $\lambda$=4602·37 Å., although difficult to resolve, had as a minimum two components.

W. E. G.

**The Absorption Spectrum of Sulphur for X-Rays.** AXEL LINDH (*Compt. rend.*, 1922, **175**, 25—27).—A study of the absorption spectra of sulphur in its different combinations shows that, as in the case of chlorine (A., 1921, ii, 344), the limits of absorption $K$ for sulphur are displaced towards the shorter wave-lengths for the higher valencies. The differences between bivalent and quadrivalent and sexavalent sulphur respectively corresponds with 7 and 11 volts. The absorption spectra of the thiosulphates offer a special interest in that they show two different limits of absorption, one corresponding with bivalent sulphur and the other with sexavalent sulphur. W. G.

**The Precise Measure of the Layers of Energy of the Barium Atom and the Appearance of the L-Spectrum of Ionisation.** A. DAUVILLIER (*Compt. rend.*, 1922, **174**, 1543—1546).—Using the method previously described (A., 1921, ii, 421, 475; this vol., ii, 463), the author has studied the high frequency spectrum of barium. The photographs show two white rays, $L_1$ and $L_2$, the positions of which coincide with those of the limits of absorption. These two rays are immediately followed by two weak black lines of slightly greater wave-length. From these rays the energy of the layers of low frequency has been measured, and for the layer $P$ the value found is $7{\cdot}0 \pm 0{\cdot}3$ volts, although the ionisation potential of barium vapour has been found to be 5·2 volts. The doublet $\gamma_2$ $\gamma_7$ has been found for barium, $\gamma_3$ being much more intense than $\gamma_7$, and each of these rays has a satellite of greater wave-length. Further, a number of weak rays have been found which are satellites of the principal rays, and certain lines of ionisation have been noted and measured. The wave-lengths of the $L$-rays for barium are tabulated and their intensities given, and amongst these are certain new lines which cannot at present be attributed with certainty to barium. W. G.

**A New Absorption Phenomenon Observed in the Domain of X-Rays.**—M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1922, **174**, 1546—1548).—The existence of absorption rays in the neighbourhood of the limits of high frequency has previously been recorded (A., 1920, ii, 655; 1921, ii, 475). A study of the $L$ emission spectrum of barium, without the interposition of any screen, has shown such rays to be much more apparent and without any absorption band being visible (preceding abstract). This phenomenon is attributed to the state of intense ionisation in which the barium atoms occupying the focus of the anticathode are found. W. G.

**Spectral Study of the Triboluminescence of Sucrose.** HENRI LONGCHAMBON (*Compt. rend.*, 1922, **174**, 1633—1634).—The spectrum of triboluminescence of sucrose shows almost all the constituents of the second positive band spectrum of nitrogen and no others. The triboluminescence of sugar is thus due to a

discharge in the air between two solid particles which have just been suddenly separated and are electrically charged. A triboluminescent effect may be obtained in a tube in which sugar has been finely powdered by shaking, the tube being evacuated by sudden compression or expansion of the residual air. W. G.

**The Fluorescence of Mercury Vapour Excited by Röntgen Rays.** J. STEPH. VAN DER LINGEN (*Z. Physik*, 1922, **10**, 38—40).—The fluorescence spectrum of mercury vapour at low densities, obtained with soft Röntgen rays, consists of two structureless bands and five emission lines. The bands reach from 4350 to 5500 and from 3100 to 3600 Å., and have their maxima at 4350 and at 3300 Å. The emission lines are 3140 Å., 3660 Å., 4050 Å., 4350 Å., and 5500 Å. The spectrum excited by Röntgen rays is in no way similar to that excited by ultra-violet light between 1860 and 2550 Å., with the possible exception of bands in the visible spectrum. In no case was any trace found of the lines 2536 and 2346 Å. discovered by Steubing (*Physikal. Z.*, 1909, **10**, 797). W. E. G.

**The Characteristic Röntgen Radiation from Carbon and Boron.** J. HOLTSMARK (*Physikal. Z.*, 1922, **23**, 252—255).—Measurements are made of the *K* radiation for boron and carbon, and these are compared with the previous values of Richardson and Bazzoni (this vol., ii, 14), Hughes (this vol., ii, 184), and Kurth (*Physical Rev.*, 1921, **18**, 461). The wave-lengths of the *K* radiation of carbon and boron are $\lambda=42{\cdot}9$ and $\lambda=83{\cdot}6$, respectively. The boron point is not in line with the $K_a$ emission points for other elements. Theoretical reasons are advanced to account for this deviation. W. E. G.

**The Chemical Action of Penetrating Radium Rays. XIV. The Action on Oxalic Acid, Potassium Tetroxalate, and Potassium Chlorate.** ANTON KAILAN (*Monatsh.*, 1922, **43**, 1—12).—When a 0·01 *N*-solution of oxalic acid was exposed for 2136 hours to the action of the rays from about 100 mg. of radium, a *considerable loss of acidity occurred* and a smaller loss of reducing power when titrated with permanganate. The radiated solution contained also formic acid and an aldehyde. The quantitative determinations showed that the greater part of the oxalic acid which disappears decomposes according to the equation $C_2H_2O_4 = CO_2 + H{\cdot}CO_2H$. Some hydrogen peroxide is formed according to the equation $C_2H_2O_4 = 2CO + H_2O_2$, and this causes the apparent loss of oxalic acid, as shown by the permanganate titration, to be smaller than the loss estimated by acidity. From previous work on the equilibrium of hydrogen peroxide under the influence of radium rays (this vol., ii, 466) it is concluded that the decomposition of the oxalic acid is not conditioned by hydrogen peroxide formation. In presence of uranium nitrate, oxalic acid disappeared at the same rate under the influence of radium rays as in its absence,

but no formic acid was found in the radiated solution. Experiments showed that the decomposition of formic acid by the rays was not accelerated by uranium nitrate, and it must be concluded that no formic acid is produced from the oxalic acid when the uranium salt is present. On the other hand, more hydrogen peroxide is formed, as shown by the permanganate titre of the radiated solution. The ratio of number of molecules affected by the rays, $m$, to number of ion pairs, $n$, is in each case 0·3, whether calculated on oxalic acid or hydrogen peroxide.

Under the influence of rays from a quartz mercury lamp, in absence of uranium salt decomposition of the oxalic acid occurred without formation of formic acid, whilst in presence of uranium salt much formic acid appeared and the permanganate titre fell more rapidly than the acidity.

When potassium tetroxalate solution was exposed to radium rays, less formic acid and more hydrogen peroxide was produced than when oxalic acid was used. The lower hydrogen-ion concentration might have led to more rapid decomposition of the formic acid. The rays from the quartz mercury lamp resulted in hydrogen peroxide formation but no formic acid; in presence, however, of uranium nitrate 1 mol. of formic acid was found for each mol. of oxalic acid disappearing.

Potassium chlorate in $0·1N$- to $0·01N$-solution undergoes very slight reduction to chloride by prolonged action of radium rays at 8—14°. After sixty-four hours' exposure at 45—50° to the rays of a quartz mercury lamp there was only slight reduction about equal to that produced by 1000 hours' exposure to radium rays. E. H. R.

**The Binding of Electrons by Atoms.** J. W. Nicholson (*Phil. Mag.*, 1922, [vi], **44**, 193—203).—A mathematical paper in which it is shown that the hyperbolic orbits of Epstein which have been used extensively in the interpretation of certain groups of $X$-rays rest on a mathematical error. A determinate and finite value of $W$ cannot be obtained for an electron moving about any atomic nucleus, if the path involved takes the electron to infinity. W. E. G.

**New Differential Method for the Measurement of the Conductivity of Electrolytes.** L. Rolla and L. Mazza (*Gazzetta*, 1922, **52**, i, 421—428).—The apparatus used in this method consists of an induction coil, $I$, a resistance box, $R$, a telephone, $T$, and three coils, $P_1$, $P_2$, and $S$, wound on an iron core. $P_1$ and $P_2$ have equal resistances and coefficients of self-induction, and the three coils together form a differential transformer with two primary circuits and one secondary.

The electrolytic resistance, $X$, to be measured is connected, in series with the induction circuit, $P_1$, to the terminals of the induction coil; the resistance box is similarly connected, in series with $P_2$, to the same terminals so that the current at any moment flows

through $P_1$ and $P_2$ in opposite directions. $S$ is connected directly to the telephone.

Consideration of the two circuits $XP_1I$ and $RP_2I$ shows that $P_1$ and $P_2$ produce at any instant two opposite magnetic fluxes, $F_1$ and $F_2$, the resultant flux being $F_1-F_2$. When $F_1-F_2=0$, the *E.M.F.* induced in $S$ is zero and the telephone is silent; this condition is evidently satisfied when $X$ and $R$ are equal. The arrangement of $P_1$, $P_2$, and $S$ on a cylindrical iron core gives poor results, but if the core consists of two L-shaped pieces juxtaposed to form a rectangle and $P_1$ and $P_2$ be wound together on one long side and $S$, composed of three separate coils capable of being grouped variously, be wound on the opposite long side of the core, excellent results are obtained. The sensitiveness of the method may be greatly increased by the use of the audion. T. H. P.

**The Electromotive Properties of Magnesium and the Potentiometric and Thermal Analysis of the System Magnesium—Mercury.** R. PH. BECK (*Rec. trav. chim.*, 1922, **41**, 353—399).—The normal potential of magnesium has not been ascertained with certainty, and as some magnesium amalgams in contact with solutions appear to yield as great a potential difference as the metal itself, the author has extended the work of Cambi and Speroni (A., 1915, ii, 453) on the thermal analysis of magnesium amalgams in an endeavour to complete the fusion diagram, to investigate the potential differences due to amalgam as compared with those due to the pure metal, and to ascertain whether the values obtained for the potential are in accord with the dilution law. The figures given by Cambi and Speroni (*loc. cit.*) for amalgams containing from 70 to 84 atomic % of mercury are confirmed; no measurements were made for higher percentages. The following compounds were found in the system: $MgHg_2$, transition temperature 170°, at which it is coexistent with MgHg; MgHg, m. p. 625°; $Mg_3Hg_2$, m. p. 562°; $Mg_2Hg$, m. p. 580°; and the thermal diagram is given and discussed in detail. The existence of $Mg_{10}Hg$, stated by Kremann and Muller, is disproved; it is suggested that their mixtures were not sufficiently heated to attain equilibrium. The vapour pressures of two amalgams were measured, but little value is claimed for the results owing to experimental difficulties; similar measurements made by Kremann and Muller are criticised for the same reason.

Determinations of the potential differences between amalgams varying from 0—60 atomic % of mercury in a solution of anhydrous magnesium chloride of 0·1982$N$-concentration in ethyl alcohol against a calomel electrode were made. The results obtained show considerable fluctuations with change of composition of the amalgam, but no conclusion is drawn that these correspond with new phases. It seems, however, that no mixture or compound of the two constituents is more negative than magnesium itself. The author points out that the usual method of preparing amalgams for such

·xperiments does not exclude the possibility of working with a netastable substance and that measurements made against aqueous olutions may give too low a value but never too high. Further, if he potential difference undergoes the normal change on dilution, his would tend to confirm the accuracy of the figure obtained. 3ut in the case of magnesium, the potential becomes less positive vith increasing dilution. In order to compare the potential of nagnesium and of magnesium amalgams in contact with neutral cid and alkaline solutions, several series of experiments were arried out in which the measurement was made in open vessels, sing a normal calomel electrode. The conclusions drawn are that he potential of magnesium may be measured in acid solution and hat the figures obtained differ but little from those for magnesium malgams, that in neutral solution atmospheric oxygen may cause he metal to be somewhat passive, and that in alkaline solution here is a considerable tendency towards passivity. In the case of nagnesium in contact with solutions of magnesium sulphate of 'arious concentrations, the results appear to contradict the .ypothesis put forward by Kistiakowsky (A., 1910, ii, 258), that nagnesium passing into solution from an electrode is primarily ransformed into the hydroxide. In acid solutions of different oncentrations, the potential becomes more negative with increasing ilution; the figure finally reached is $E_H = -1{\cdot}854$. Experiments n cathode polarisation of magnesium showed that measurements f potential made after interruption of the polarisation are never nore negative than the highest values obtained for the metal and rom its amalgam with no current passing. Thus this last figure hould be considered as very close to the equilibrium potential which he author suggests is most probably $E_H = 1{\cdot}856—1{\cdot}876$ volts.

H. J. E.

**Absorption of Hydrogen by Elements in the Electric Discharge Tube.** F. H. NEWMAN (*Phil. Mag.*, 1922, [vi], **44**, ·15—226).—A further study of the behaviour of hydrogen in the resence of various elements in a discharge tube (cf. A., 1921, ii, 295). Evidence is obtained that the "clean up" of hydrogen in a discharge tube is partly due to chemical changes. On the admission f hydrogen, activated by an electric discharge, to the clean surface f a sodium–potassium alloy a white, crystalline compound was roduced which was probably composed of the hydrides of the two netals. The white layer slowly changed to a dark grey deposit. Similarly, the activated gas gave hydrogen sulphide with sulphur. These effects were not due to the ions of the discharge tube, as these were eliminated by charged platinum strips before the gas reached ither the alloy or the sulphur. Measurements were made of the ates of disappearance of hydrogen in the presence of sodium–potassium alloy, and of sulphur and other elements. A considerable roportion of this absorbed hydrogen was recovered when the tube vas heated at 300°. Nitrogen, on the other hand, cannot be again iberated, even when the tube is heated to the softening point. The

modifications of hydrogen and nitrogen which are absorbed in the discharge tube are probably triatomic.

The absorption is not entirely due to chemical action, for the law of constant proportions does not appear to be followed.

W. E. G.

**Rapid Electrolysis without Rotating Electrodes.** Graham Edgar and R. B. Purdum (*J. Amer. Chem. Soc.*, 1922, **44**, 1267—1270).—Rapid electrolysis may be carried out without the use of rotating electrodes if the solution is stirred by means of a current of air. A piece of apparatus is described for such analyses. The cathode is a platinum gauze cylinder in the centre of which is a spiral platinum electrode. The electrodes are contained in a glass tube 31 mm. diam. to which are sealed three glass "air lifts," connected in a single tube at the bottom and entering symmetrically about half-way up the wide tube, the seals being made tangentially. When air is forced into the apparatus half filled with liquid, both vertical and rotational stirring is effected. Experiments are described which show that the results obtained with this apparatus are equally as good as those obtained with rotating electrodes.

J. F. S.

**An Electrochemical Study of the Reversible Reduction of Organic Compounds.** J. B. Conant, H. M. Kahn, L. F. Fieser, and S. S. Kurtz, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1382—1396).—The authors have developed the general equation $\pi = \pi'_0 + 0{\cdot}0295 \log ([A]/[AH_2]_r - 0{\cdot}0295 \log K_1K_2 + 0{\cdot}059 \log [H^+] + 0{\cdot}0295 \log \{K_1(K_2 + [H^+]/[H^+]^2) + 1\}$ (in which A represents the oxidised and $AH_2$ the reduced form) to express the oxidation-reduction potentials of compounds of the type of quinone in both acid and alkaline solutions. The potentials of six anthraquinonesulphonic acids have been measured by a titration method, using titanous chloride and sodium hyposulphite, and the results obtained over a wide range of hydrogen-ion concentration have been found to be in accord with the above equation. The validity of the method is shown by determinations of the potentials of mixtures of the reduced and oxidised compounds.

W. G.

**Thermo-regulator.** E. B. Starkey and N. E. Gordon (*J. Ind. Eng. Chem.*, 1922, **14**, 541).—A thermo-regulator is described which is capable of giving a steady temperature to 0·05°. The regulator consists of a U-tube, connected through a short vertical capillary with a toluene container. The U-tube and capillary are filled with mercury, the two ends of which are connected with wires which form one of the leads of the heating lamp. Expansion of the toluene causes the mercury to be pushed away from one wire and so break the circuit, whilst contraction remakes the circuit. Corrosion of the mercury is prevented by filling the space above the mercury with an inert gas.

J. F. S.

**Entropy of the Elements and the Periodic System.** W. HERZ (*Z. Elektrochem.*, 1922, **28**, 258—259).—A theoretical paper in which the author shows that the entropy of the elements varies regularly in keeping with the arrangement of the elements in the periodic system. Using the entropy values calculated by Lewis and Gibson (A., 1918, ii, 29), it is shown that in any group of the periodic system the value of the entropy increases with increasing atomic weight in the case of the metallic elements, the elements of the fourth group and the inactive gases, whilst the electronegative elements of the oxygen and halogen groups have decreasing entropies with increasing atomic weights. J. F. S.

**Proposal for the Fixing of a Unit of Measurement in Thermochemistry.** W. SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, **1**, 479—487; cf. A., 1921, ii, 679).—The following proposals were put forward at the International Chemical Conference at Brussels in 1921. The heat of combustion of 1 gram of benzoic acid, in cal. at 15°, should be taken as the unit, rather than that of cane-sugar, which is hygroscopic, or of naphthalene, which is liable to sublime. By using one substance only for the standard, many constant calorimetrical corrections would not be needed, and a simpler formula could be used. Certain discrepancies in the values for the heat of combustion of benzoic acid, as obtained by various workers, are pointed out, and also in the ratios for the heats of combustion of benzoic acid, cane-sugar, and naphthalene. It is proposed that the heat of combustion of benzoic acid at constant volume be taken provisionally as 6321 cal., with the proviso that the determination of this value be repeated as soon as possible, with the greatest possible accuracy, using the method of adiabatic measurements. R. T.

**Temperatures of Combustion.** J. BRONN (*Z. angew. Chem.*, 1922, **35**, 328).—The temperature of combustion of a gas is calculated from the heat of combustion and the specific heat of the products of combustion. An accepted figure for the combustion of hydrogen in pure oxygen is 6670°, which would presume the specific heat of steam to be 0·485. It is shown that the specific heat at 4000° may be taken at 0·85, from which the temperature of combustion may be calculated to be 3900°. The temperatures for carbon monoxide (5000°), methane (4400°), and acetylene (6200°) are given. The temperatures of combustion of gases are greatly influenced by their velocities of flame propagation, except in so far as flameless combustion affects the result. The velocities of flame propagation of ethylene, acetylene, and benzene differ. H. M.

**Thermochemical Researches on Oximes. I. Ketoximes not Exhibiting Stereoisomerism.** ALICJA DOBABIALSKA (*Roczniki Chemji*, 1921, **1**, 424—447).—The heats of certain reactions of some ketoximes are measured. From the results so obtained, and from those obtained previously (W. Swientoslawski, A., 1919, 2, 336), various generalisations are made. The ketoximes used were

acetoxime, phenylmethylketoxime, and diphenylketoxime. The chief reactions studied are the formation of the hydrochloride of the oxime, its solution in 10% sodium hydroxide solution, and the formation of the sodium salt of the oxime. The results obtained, together with those calculated from these, are given in the following table, where $q_{HCl}$ is the heat of formation of the hydrochloride, in ethereal solution. For aqueous solution this is expressed by $q'_{HCl}$. The heat of the solution of the hydrochloride in 10% sodium hydroxide solution is $Q_{HCl}$, in water, $S_{HCl}$. The heat of solution of the oxime in dilute sodium hydroxide solution is $q$, in water, $S$, in ether, $S'$. The degree of hydrolysis of sodium salts of these oximes is given as $\nu$%. Results are expressed in calories per millimole.

| | $q_{HCl}$ | $q'_{HCl}$ | $q$ | $\nu$% | $Q_{HCl}$ | $S$ | $S_{HCl}$ | $S'$ |
|---|---|---|---|---|---|---|---|---|
| Acetoxime | 10·93 | 1·19 | 5·70 | 39·6 | 17·16 | −1·28 | −1·95 | −2·89 |
| Phenylmethyl-ketoxime | 8·17 | 0·51 | 6·34 | 40·3 | 16·52 | −2·98 | −3·52 | — |
| Diphenyl-ketoxime | 7·71 | — | 5·80 | — | 12·51 | −4·06 | −6·99 | — |

In the case of phenylmethylketoxime, the hydrochloride, prepared at different temperatures, and from different media, gave the same $Q_{HCl}$, thus showing that no stereoisomeric modification of this oxime is produced under the conditions in question.

It is concluded that the heat of formation of the hydrochlorides of the ketoximes differs little from that of the aldoximes, and diminishes as the acidity of the ketoxime increases. The heat of solution of these hydrochlorides diminishes with increasing acidity of the ketoxime, owing to a parallel increase in the negative heat of the solution, and decomposition of the former in water. Finally, the negative heat of solution of ketoximes in water appears to be greater than that of aldoximes. R. T.

**Pycnometry.** R. SAAR (*Chem. Ztg.*, 1922, **46**, 433—435).—Tables and formulæ are given for calculating specific gravities from one temperature to another. W. P. S.

**An Experimental Comparison of the Viscous Properties of (*a*) Carbon Dioxide and Nitrous Oxide; (*b*) Nitrogen and Carbon Monoxide.** C. J. SMITH (*Proc. Physical Soc.*, 1922, **34**, 155—164).—The viscous properties of these gases have been compared directly by observing the time required by a mercury pellet to force a certain volume of the different gases through a capillary tube. Measurements were carried out at different temperatures, absolute viscosities were obtained by comparison with air, and the mean area of collision deduced by using Chapman's formula.

The viscosities expressed in C.G.S. units $\times 10^{-4}$ are: carbon dioxide and nitrous oxide, 0·0°, 1·366; 15·0°, 1·441; 100·0°, 1·845. Carbon monoxide and nitrogen, 0°, 1·665; 15·0°, 1·737; 100·0°, 2·118. The mean collision areas in square centimetres are: carbon dioxide and nitrous oxide, $0·834 \times 10^{-15}$. Carbon monoxide and nitrogen, $0·767 \times 10^{-15}$.

The fact that carbon dioxide and nitrous oxide (or carbon monoxide and nitrogen) have molecular dimensions which are identical within experimental error is consistent with Langmuir's view that the outer electron arrangements of these molecules are the same; this is also supported by the fact that the viscosities are equal at the three temperatures chosen. W. T.

**Theory of Adsorption Processes.** A. EUCKEN (*Z. Elektrochem.*, 1922, **28**, 257—258).—Polemical; an answer to Polanyi's criticism (this vol., ii, 479) of the author's paper on the theory of adsorption processes (this vol., ii, 262). J. F. S.

**Adsorption in Solution and at Interfaces of Sugars, Dextrin, Starch, Gum Arabic, and Egg-albumin, and the Mechanism of their Action as Emulsifying Agents.** GEORGE L. CLARK and WILLIAM A. MANN (*J. Biol. Chem.*, 1922, **52**, 157—182).—Measurements were made of the surface tension and viscosity of solutions of the above substances for a large number of concentrations both with and without the addition of electrolytes. The interfacial tension between each solution and benzene was also measured, and the efficiency of the emulsifying agent with respect to both benzene and kerosene estimated. The factors of predominating importance in an emulsifying agent appear to be viscosity and ability to lower interfacial tension. In the case of sugar, viscosity is the more important, whilst with egg-albumin, which gave the best emulsions, film formation is of primary importance. Two types of agglomeration are distinguished, namely, that accompanied by an increase in viscosity, in which coalescence of the particles is accompanied by enclosure of water, and that producing a decrease in viscosity, in which there is a decrease both in surface and amount of bound water. Dextrin and starch, considered separately, provide examples of the former type. When these substances are considered in relation to one another, however, it is found that the viscosity curves run parallel, the curve for dextrin being slightly above that for starch, thus resembling the viscosity curves of sulphur sols of different degrees of dispersion (cf. Odén, A., 1912, ii, 1143). This is considered to be evidence that starch and dextrin differ merely in the degree of agglomeration (second type) of the particles, and thus to furnish experimental proof of the view put forward by Herzfeld and Klinger (A., 1920, i, 713). E. S.

**Carrying Down by Precipitates.** PAUL DUTOIT and ED. GROBET (*J. Chim. physique*, 1922, **19**, 328—330).—The carrying down of soluble salts by precipitates is explained by the authors as due to the fact that the adsorption of these substances on the surface of the precipitate causes the soluble substance to attain locally a value which exceeds its solubility product and hence causes its precipitation. With the object of testing this hypothesis, the author has estimated calcium in the presence of magnesium

salts as oxalate, and barium in the presence of calcium both as sulphate and chromate. Two series of experiments were carried out, in the first stirring by hand with a glass rod was employed, and in the second series very rapid mechanical stirring was used. Very different results were obtained in the two series, but the values of the second series are in good agreement with the theoretical values, thus showing that soluble substances are not appreciably carried down by precipitates if the solution is rapidly stirred during the mixing. J. F. S.

**The Sorption of Neutral Soap by Wool, and its Bearing on Scouring and Milling Processes.** BRITISH RESEARCH ASSOCIATION FOR THE WOOLLEN AND WORSTED INDUSTRIES (*Trans. Text. Inst.*, 1922, **13**, 127—142).—The sorption of soap from aqueous solution by carefully cleansed wool at 25° has been studied. Analyses of the solution were made after an arbitrarily fixed interval, without waiting for equilibrium to be established, and corrections were applied for the amount of water sorbed by the wool on the assumption that the material contains 15% of moisture under ordinary atmospheric conditions and 33% when immersed. The results indicate preferential sorption of the kation, and it is suggested that the fatty acid is removed from solution both by sorption and by precipitation on the fibre. With mixtures of soaps of oleic and palmitic acids, preferential sorption of oleic acid occurs, but the potassium and sodium oleates are almost identical in behaviour. The effect of the fatty acid is apparently to lower the sorption of alkali. J. C. W.

**Mordants. I.** WILDER D. BANCROFT (*J. Physical Chem.*. 1922, **26**, 447—470).—A historical review of the use of mordants in dyeing. J. S. G. T.

**The Dissociation of Barium Platinichloride.** G. GIRE (*Compt. rend.*, 1922, **174**, 1700—1703).—The author has measured the dissociation pressures of barium platinichloride over the temperature range 428° to 665°, and has obtained the equation

$$\log P = -3446{\cdot}316/T + 7{\cdot}702 \log T - 17{\cdot}41669.$$

The dissociation of barium platinichloride is an equilibrium of the type, sol. + gas $\rightleftharpoons$ sol. + $Q$, and the value of $Q$ is calculated to be 30·35 cal. for the temperature 948°, which corresponds with a pressure of 760 mm. W. G.

**A Rapid Dialyser.** A. GUTBIER, J. HUBER, and W. SCHIEBER (*Ber.*, 1922, **55**, [*B*], 1518—1523).—The apparatus consists of a wooden disk supporting a framework composed of glass rods in the form of a hollow cylinder. The membrane is passed over the framework and secured in its natural folds to the wooden disk. A stirrer is placed within the vessel, which is mounted in such a manner that the frame and stirrer can be rotated in opposite directions (the apparatus is fully figured in the original). The

apparatus is placed in an inverted, tubulated bell-jar, through the tubulus of which water is admitted, which can be heated or cooled by coils placed in the jar; the level of the water and its discharge are governed by a lever arrangement. Comparative experiments show the dialyser to be much more rapid in its action than those of Graham and Zsigmondy-Heyer. In addition to rapidity of action, the following advantages are claimed for the apparatus: extensive exclusion of external air from the internal liquid, from which, however, samples may readily be taken; small liability to changes in volume, particularly to dilution of the internal liquid; great safety in action, since only a single piece of parchment is used; simple method of securing a continuous change of external water; the possibility of dialysis at raised or lowered temperatures without complicated arrangements. H. W.

**Dolezalek's Theory of Solutions.** K. HERRMANN (*Z. angew. Chem.*, 1922, **35**, 349—351, 353—355).—A theoretical paper in which liquid mixtures and solutions are differentiated and discussed generally and in connexion with the Dolezalek theory of solutions. J. F. S.

**Measurement of Solubility by Floating Equilibrium. Solubility of Lead Acetate.** MERLE L. DUNDON and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1196—1203).—A new method for the determination of solubility is described. The method consists in placing a float, which has been calibrated so that it will just sink in a solution of known composition of the substance under investigation, into a weighed quantity of the saturated solution and adding the solvent until the float just sinks. The quantity of solvent added is noted, and from this, the weight of the solution taken, and the calibration constant of the float the solubility is readily calculated. This method has been applied to the determination of the solubility of lead acetate in water at temperatures from 0° to 50°. The following values in grams of lead acetate per 100 grams of water are recorded: 0°, 19·7; 5°, 23·7; 10°, 29·3; 15°, 35·6; 20°, 44·3; 25°, 55·2; 30°, 69·7; 35°, 88·9; 40°, 116·0; 45°, 153·0; 50°, 221·0. The method is capable of considerable speed or great accuracy, and in ordinary circumstances of a considerable amount of both. Some variation is found in duplicate experiments at the higher temperatures, which is shown to be due to the hydrolysis of the acetate followed by subsequent evaporation of acetic acid. J. F. S.

**Influence of Electrolytes on the Solubility of Non-electrolytes.** ANDREW MCKEOWN (*J. Amer. Chem. Soc.*, 1922, **44**, 1203—1209).—The heats of solution of ether in various solutions of sodium chloride have been calculated from Thorne's solubility data at 15° and 25° (T., 1921, **119**, 262), by means of an expression which connects solubility, heat of solution, and temperature, of the form of the van't Hoff isochore. Statistical

:eatment of the phenomena of solution and precipitation leads ɔ an expression for solubility, $S = Ae^{Q/RT}$, which is in agreement ith the isochore relation mentioned above. The salting-out effect f salt on ether has been examined so far as the effect depends on he activities of the ions of the salt. It is shown that the relative pecific influences of the kation and anion are −21·7 and +671, hat is, the anion is the predominating factor in the process.

J. F. S.

**Amorphous Precipitates and Crystalline Sols.** F. HABER Ber., 1922, **55**, [B], 1717—1733).—The method of distinguishing etween the crystalline and amorphous condition depends on the bility of crystalline substances to give Röntgen-ray interference ·inges. The trustworthiness of the method is dependent on the onditions (1) that the lattice constants are not less than the half ʼave-length of the Röntgen rays employed, (ii) that they are not ıuch greater, and (iii) that the material under investigation is niform in its lattice properties.

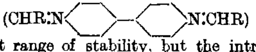
Crystalline or amorphous, solid masses are obtained by superaturation processes which may be considered to occur in two istinct phases, the formation of aggregates and the rearrangement f such aggregates, with loss of free energy, into ordered lattice ɔrmations. The former process can be studied conveniently in upercooled, molten masses of a uniform chemical material which ıay be regarded as unarranged molecular aggregates the further ıte of which depends on their rate of arrangement. With regard ɔ the process of arrangement, its energy is known (latent heat of quefaction), and also that it is divisible into two parts, the formaion of nuclei and their growth. Tammann's work on this subject as shown that the formation of nuclei frequently only occurs ʼith considerable velocity at temperatures far below the melting oint at which the nuclei can only grow very slowly; if, however, he mass is heated to just below its melting point, the nuclei grow apidly and crystallisation occurs throughout the entire mass. 'hermodynamical treatment of the subject shows that the minute ggregates are only stable when the condition is fulfilled that $\Delta T/T = 2S/rqd$, in which $\Delta T/T$ is the fraction of the mass melting oint $T$ in absolute values by which cooling must occur if the ɔlid phase, regarded as spheres of radius $r$, is to be in (labile) quilibrium with the molten mass. $S$ is the specific free energy f the boundary surface, $q$ the latent heat, and $d$ the density of he solid phase.

The processes involved in the formation of precipitates and sols iffer from those described above in that the rate of aggregation an be controlled by exceeding the limit of solubility to a greater r less extent. The connexion between the mass solubility $H_M$ ıolubility as generally accepted) and the solubility of the smallest ggregates, $l$, is given by the equation $2S'M/rd = RT \log l/L_M$, ı which $S'$ is the specific free surface energy of the particles, $T$ the ɜmperature of the experiment, $d$ the density of the solid phase,

*M* the molecular weight, and *r* the radius of the particles regarded as spheres.

The considerations outlined above are applied to the formation of very sparingly soluble substances. If the rate of aggregation is high and as far as possible in excess of that of arrangement, amorphous precipitates are to be expected which gradually, particularly on warming, pass into the crystalline condition. If, however, the rate of aggregation is depressed by only slightly exceeding the solubility limit, the rate of arrangement may be sufficient to cause the orderly formation of crystals before the formation of visible particles has occurred. This, however, involves an alteration in the rate of aggregation due to electrical phenomena at the boundary of the molecules and liquid, the net result of which is that the growth of the aggregates is greatly impeded and sols are produced. These conclusions are illustrated by the cases of the precipitates and sols of aluminium or ferric hydroxides which, however, are to be regarded as the ideal case from which deviations are to be expected in two directions. If the rate of arrangement is greater, it is not to be expected that the precipitate will be obtained in the amorphous condition and be retained as such during the Röntgen exposure. The rate of arrangement may be expected to be at its maximum in binary, heteropolar compounds in which the bipolar character is most marked. (This is illustrated in the cases of the silver haloids and the sulphides of mercury, zinc, and cadmium). On the other hand, with molecules in which the bipolar character is not strongly accentuated, the tendency towards the formation of amorphous sols and precipitates must be more marked; this is illustrated experimentally by the cases of the hydroxides of zirconium and thorium. H. W.

**Molecular Arrangement and Liquid Crystal Formation.** D. VORLÄNDER (*Z. angew. Chem.*, 1922, **35**, 249—250).—A close relationship is shown to exist between the symmetry of the molecule and its capacity to form liquid crystals. This property is shown to the greatest extent by those molecules containing long chains of atoms and possessing a definite axis of symmetry. Thus para-substitution in the benzene ring is especially favourable to the formation of liquid crystals. The introduction of groups which destroy the symmetry of the molecule either reduces the range of stability or else completely destroys the power of formation of liquid crystals.

Benzidine derivatives  give liquid crystals with a great range of stability, but the introduction of a $CH_2$ group between the two benzene nuclei causes the disappearance of this enantiotropic form. On account of the angle between the carbon valencies (109° 28′) the molecule will no longer be symmetrical. Similar results are obtained by the introduction

›f CO, CS, S, and O groups into the same position. The NH group ·educes the range of stability practically to zero, although nonotropy is sometimes observed in these compounds. Further engthening of the chain with the formation of diphenyl ethane lerivatives causes a reappearance of the property, although it is ıot so strongly developed as in the diphenyl derivatives. The liphenylpropanes do not yield liquid crystals, which, however, ‚ppear again with the derivatives of diphenylbutane. The author ›xplains these phenomena by the departure of the molecule from the traight line arrangement. W. E. G.

**Electrical Precipitation of Colloids.** CLAUDE HAINES IALL, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1246—1249).—Finely ivided suspensions of arsenious sulphide, mercuric sulphide, russian blue, barium sulphate, aluminium, copper, lead, silver, nd iron, in transformer oil of resistance $1{\cdot}5 \times 10^{16}$ ohms per c.c., ave been subjected to alternating and direct currents of voltages rom $10^4$ to $2 \times 10^5$ with the object of effecting a precipitation. n no case was any precipitation brought about, even although the urrent was applied for three hours. A theoretical treatment of he subjects shows that the rate of precipitation would be 1/20000 f that for smoke for the same application of energy. J. F. S.

**A Static Method of Study of Hydration.** MARCEL GUICHARD *Bull. Soc. chim.*, 1922, [iv], **31**, 552—554).—A simple form of appar- tus is described in which it is possible to follow the equilibrium etween an absorbent substance and water vapour in a vacuum nd over a fairly considerable range of temperature. It consists f a glass tube to contain the absorbent substance and having ealed to it at right angles a graduated tube which contains the vater. The whole is evacuated and sealed off. The two parts f the apparatus can be maintained at different temperatures s desired. W. G.

**The Geometric Representation of Saline Equilibria.** IENRY LE CHATELIER (*Compt. rend.*, 1922, **174**, 1501; cf. A., 894, ii, 223).—A reaffirmation of priority in the method of re- resenting saline equilibria by square diagrams as opposed to he claim of Jänecke (this vol., ii, 427). W. G.

**Effect of an Electrolyte on Solutions of Pure Soap. Phase-rule Equilibria in the System Sodium Laurate–Sodium Chloride–Water.** JAMES WILLIAM MCBAIN and ARTHUR OHN BURNETT (T., 1922, **121**, 1320—1333).

**The System Silver Perchlorate–Water–Benzene.** ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1922, **44**, 1163—1193; cf. A., 921, ii, 261).—The ternary system silver perchlorate–water–benzene and the binary systems made up of pairs of the components ave been investigated. It is shown that the system silver per- hlorate–water has a eutectic point at $-58{\cdot}2°$, at which temperature he saturated solution contains 73·9% of the silver salt. This is

the lowest eutectic known for a true salt and water. The solubility of silver perchlorate rises to 88·8 % at 99°. The eutectic of silver perchlorate–benzene is at + 5·12° and the solution contains 3·44 % of the silver salt. The solubility curve rises steeply with the temperature, reaching an almost perpendicular form between 50° and 145°; at the latter temperature the saturated solution contains 63·0 % of silver perchlorate. Attention is directed to the similarity between this solubility curve and those which are found where the system gives rise to two liquid phases, either in the stable or metastable region. The hydrate $AgClO_4,H_2O$ has been isolated and its transition temperature found to be 43·1°; the compound $AgClO_4,C_6H_6$ has also been isolated and its transition point found to be 145°. The ternary system, silver perchlorate–water–benzene is marked by the possession of six realisable invariant equilibria, and a very large number of univariant equilibria, which furnish at least one example of every type of equilibrium theoretically possible for a ternary system containing volatile components. The ternary eutectic representing three solid phases, solution, and vapour, lies at − 58·4°, and the eutectic of highest temperature is at 42·1°. The course of the twenty-four univariant equilibria originating at these two quintuple points and the four intermediate quintuple points has been investigated. Isothermal diagrams have been constructed to show the various equilibria existing at temperatures between − 58·4° and + 145°. Between 5·24° and 23·4° three coexistent liquid phases can be prepared in stable equilibrium with each other and their vapour. The occurrence of two separate fields of unsaturated solution is explained as due to the intersection of the solubility curve of silver perchlorate with the binodal curve representing the limited solubility of benzene and water. The occurrence of a third field is explained as due to the existence, between − 2·7° and + 30°, of an additional closed bi-nodal curve which does not extend to any one of the two component axes at any temperature. It appears that this is the first demonstrated case of a closed bi-nodal curve. J. F. S.

**Use of Iron Pyrites in a Friedel–Crafts' Reaction.** JOHN ARMSTRONG SMYTHE (T., 1922, **121**, 1270–1279).

**Combination in Detonating Gas in Presence of Colloidal Palladium Solution.** C. SANDONNINI and A. QUAGLIA (*Gazzetta*, 1922, **52**, i, 409–416; cf. this vol., ii, 557).—In mixtures containing only hydrogen and oxygen, the reaction in presence of colloidal palladium solution is proportional to the concentration of the detonating mixture. If, however, this concentration is the same in two cases, the velocity of reaction is somewhat the greater when the hydrogen is in excess than when the oxygen is in excess. Since it is also found that the reaction of combination in pure detonating gas may be accompanied by phenomena of reduction or hydrogenation, the conclusion is drawn that in this case the combination is due to the action of active hydrogen.

The hydrogenation of ethylene and the formation of water have velocities of the same order when the ratio between the amounts of hydrogen and oxygen is that normal to detonating gas. When ethylene and oxygen are in concentrations requiring the same quantity of hydrogen and the latter is present in sufficient amount for both reactions, the latter proceed with almost equal velocities; when, however, the amount of hydrogen is insufficient for either reaction, only the formation of water occurs to an appreciable extent. T. H. P.

**Limits for the Propagation of Flame in Vapour-Air Mixtures. I. Mixtures of Air and One Vapour at the Ordinary Temperature and Pressure.** ALBERT GREVILLE WHITE (T., 1922, **121**, 1244—1270).

**Limit of Inflammability of the Vapours of the System, Alcohol-Petrol, and of a Triple System with a Basis of Alcohol and Petrol.** ROGER G. BOUSSU (*Compt. rend.*, 1922, **175**, 30—32).—A study of the variation of the lower limit of inflammability of the binary system petrol-alcohol and of the ternary system petrol-alcohol-ether, using the method of Le Chatelier and Boudouard (A., 1898, ii, 574). The results verify the formula $n/N + n'/N'=1$, where $N$ and $N'$ are the limits of inflammability of each of the two vapours and $n$ and $n'$ the proportions in which they are present in the mixture under examination. W. G.

**A Study of the Rate of Saponification of Oils and Fats by Aqueous Alkali under Various Conditions.** MABEL HARRIET NORRIS and JAMES WILLIAM MCBAIN (T., 1922, **121**, 1362—1375).

**Behaviour of certain Metals as Catalysts. I.** C. SANDONNINI (*Gazzetta*, 1922, **52**, i, 394—408).—The author has carried out a number of series of experiments with the object of ascertaining the behaviour of a catalyst, highly active in the case of two separate, analogous reactions, when it is introduced into a system in which both these reactions can occur. The catalysts employed were platinum black, reduced nickel, copper, and silver, and the systems were composed of hydrogen and oxygen, mixed with either ethylene, or phenanthrene, or nitrobenzene, or allyl alcohol, these being compounds able to undergo ready oxidation or hydrogenation.

In the system, $C_2H_4 : H_2 : \frac{1}{2}O_2$, the possible reactions are: (1) formation of water from the hydrogen and oxygen, (2) hydrogenation of the ethylene, (3) oxidation of the ethylene, and (4) decomposition of the ethylene. In presence of finely divided nickel, reaction (1) becomes explosive at the ordinary temperature, (2) becomes appreciable at 30° and has its optimum at 130—250°, whilst (3) is not markedly influenced, its products being essentially water and carbon dioxide. The results now obtained show that the velocity of reaction (1) is diminished enormously by the presence of ethylene, although at the ordinary temperature this reaction is the only one

taking place to an appreciable extent; when the temperature is raised, reaction (2) assumes an increased velocity, so that most of the ethylene is hydrogenated to ethane at 225°, and reaction (3) also becomes of measurable velocity. Various possible causes of the alternations in the velocities of reactions (1) and (2) are discussed. The retardation of reaction (1) by ethylene is analogous, up to a certain temperature, to the similar effect observed by Henry (*Phil. Mag.*, 1836, **65**, 329) for carbon monoxide, with which oxygen combines more rapidly than with hydrogen in presence of platinum. The presence of atomic or active hydrogen produced either, as Sabatier supposed, by way of a hypothetical hydride or in some other way, is insufficient to explain the author's results, which may, however, be determined in some degree by the specific adsorption of gases by metallic catalysts studied by Taylor and Burns (A., 1921, ii, 630). The possible formation of an unstable compound of nickel and ethylene, analogous to the formation of nickel tetracarbonyl from nickel and carbon monoxide, is also discussed.

In presence of copper, the velocities of the different reactions are only slightly increased, the greatest velocity at all temperatures being that of the formation of water; the copper undergoes marked oxidation, which favours oxidation phenomena. None of the reactions is appreciably accelerated by the presence of silver. The formation of water under the influence of platinum is retarded by the presence of ethylene, but is the principal reaction taking place. In the system containing nitrobenzene, the reduction of the latter in presence of nickel is more rapid than the formation of water from its elements. The results of Bone and Wheeler (T., 1904, **85**, 1637) are discussed.

T. H. P.

**Catalytic De-hydroxidation of Formic Acid.** ERICH MÜLLER [with K. SPONSEL] (*Z. Elektrochem.*, 1922, **28**, 307—310).—The catalytic conversion of formic acid into hydrogen and carbon dioxide, by means of rhodium, first studied by Deville and Debray in 1874, is due to the presence of impurities in the catalyst, the catalytic activity decreasing as the purity of the metal increases. Osmium exhibits considerable catalytic activity, and a detailed investigation has been made of the dependence of the activity on the mode of preparation of this catalyst, more especially on the temperature of reduction of the metal, the composition of the catalysed solution as regards the concentration of the acid and the presence or absence of sodium formate, and the mass of catalyst employed. Osmium prepared by reduction of the hydrated dioxide at 150° possesses very considerable activity, 0·3 gram effecting the evolution of 10 litres of gas in three hours. The activity is increased by any conditions favouring the existence of the catalyst in the colloidal state.

J. S. G. T.

**The Use of the Oxides of Platinum for the Catalytic Reduction of Organic Compounds. I.** V. VOORHEES and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, **44**, 1397—1405).—When

chloroplatinic acid is fused with sodium nitrate a brown oxide of platinum is obtained which is an excellent catalyst for the reduction of various types of organic compounds. The speed of reduction with this catalyst is greater than when ordinary platinum black is used. The most satisfactory conditions for preparing this oxide in its most active form have yet to be worked out. W. G.

**Effect of a Magnetic Field on Catalysis by Ions in the Presence of a Paramagnetic Salt.** WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN (T., 1922, **121**, 1298—1299).

**Analysis of the Electronic Structure of the Elements.** A. DAUVILLIER (*J. Phys. Radium*, 1922, [vi] **3**, 154—180).—A further discussion of the theory of atomic structure (cf. A., 1921, ii, 475, and this vol., ii, 43). A new arrangement of the periodic table is proposed which conflicts with the chemist's view as to the positions of the elements of the manganese and iron groups in the periodic table. The spectra and atomic volumes of these elements are in accord with the view that they should be placed, together with oxygen, in the sixth group. They should possess only six electrons in the outer shell of the atom. This would remove certain anomalies present in the modern theory of the periodic table. An arrangement of the electrons in the shells is advanced which differs in some respects from that of Langmuir. The maximum number of the electrons in the successive shells of the atom are respectively 2, 8, 18, 18, 32, 8 instead of 2, 8, 8, 18, 18, 32 according to Langmuir. An apparatus is described by which the author has measured the *K*, *L*, and *M* series of the heavy elements. These results, which will be communicated in a future paper, throw light on the distribution of the electrons in the various shells of the atom. W. E. G.

**Complex Compounds.** A. MAGNUS (*Physikal. Z.*, 1922, **23**, 241—247).—A theoretical paper in which the theory of Kossel (A., 1916, ii, 243) is applied to the stability relations and the valency forces of complex compounds. On this theory, the most stable complex is one which is formed from its components with the greatest liberation of energy. The case of positively charged central atoms is considered. The stability of a complex is dependent on the number of positive charges ($n$) on the central atom and on the number of groups ($p$) held in combination. It is shown that the stability of complexes with different values of $n$ and $p$ may be derived from purely electrostatic considerations. Maximum values are found for the stability at values of $p$ which are in agreement with experience. For complexes with a small charge on the central atom, high co-ordination numbers are not to be expected unless the groups attached are bipolar in nature. Ions of the form $XO_6$, in consequence of the energy conditions, are rarely stable. The stability of hydrates and compounds with ammonia is shown to

be dependent on the bipolar nature of the water and ammonia molecules. W. E. G.

**The Electron Theory of Valency as Applied to Organic Compounds.** JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1922, **44**, 1293—1313).—A theoretical paper in which the author discusses the relative merits of the theories of polar and non-polar valencies in organic compounds as applied to various types of compounds. In the molecular rearrangement of *s*-bistriphenylmethylhydrazine the theory of polar valencies gives an evident cause for the rearrangement, revealing a "fault" in the molecule, and expresses the intramolecular oxidation and reduction characteristic of the rearrangement. This theory is also applicable to the analogous molecular rearrangements of chloro- and bromo-amides, of hydroxylamine derivatives, and of peroxides. In the absorption reactions of carbon dioxide and of a large number of organic compounds containing unsaturated groups of the types C:C, C:S, C:N, polar valencies are recognised as the directing forces. The same applies to ethylene hydrocarbons.

The author develops the Crum Brown–Gibson rule of substitution in the benzene series from a polar electronic structure for benzene, which does not require the assumption of negative hydrogen, but is based on the application to benzene of results firmly established in the aliphatic series. The different behaviour of negative halogen, in compounds of the type RX, and of positive halogen, in compounds of the type RNHX, is taken as further evidence in support of polar valencies.

Evidence of the complete polar structure of acids, such as sulphuric, phosphoric, or organic acids is found in (*a*) Faraday's observation of the deposition of sulphur at the negative electrode in the electrolysis of concentrated sulphuric acid, (*b*) the work of Bird and Diggs (A., 1914, ii, 614) on the use of yellow phosphorus as the equivalent of a metal for the production of an electric current, (*c*) the production of currents by the use of organic compounds as the source of escape of electrons in oxidation-reduction cells.

In the oxidation and reduction of organic compounds at the ordinary temperature, exposed valencies on double and triple bonds, in bivalent and tervalent carbon, etc., are the common seat of oxidation and reduction reactions. Although polarity in organic compounds is insisted on as giving an invaluable guide in following organic reactions, it need not be of the extreme character shown by common salts, but may well be of the character proposed by Bohr, Lewis, and Kossel, where the transfer of electrons from atom to atom is not so complete as in the case of common electrolytes.

W. G.

**A Discussion of Triple Salts.** HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], **4**, 27—30).—In some cases where analogous triple salts are known, these occur in extensive series, but there are a great many cases where analogy is lacking between salts of analogous

etals, and there appear to be no definite laws, based on the valency : other characters of the constituent salts, according to which they :e formed. A number of examples of triple chlorides, thiocyan- ;es, and nitrites are quoted. E. H. R.

**New Small Autoclave for Hydrolysis Experiments.** .. EBERHARD GROSS (*Z. physiol. Chem.*, 1922, **120**, 185—188).— description of a small autoclave which can be heated and cooled uickly. It is therefore suitable for hydrolysis experiments in hich samples need to be withdrawn at different times for testing or various reactions. S. S. Z.

## Inorganic Chemistry.

**The Rectilinear Diameter of Hydrogen.** E. MATHIAS, ). A. CROMMELIN, and H. KAMERLINGH ONNES (*Ann. Physique*, .922, **17**, 463—474).—A *résumé* of work already published (A., .921, ii, 256; this vol., ii, 440). W. G.

**The Rectilinear Diameter of Oxygen.** E. MATHIAS and H. KAMERLINGH ONNES (*Ann. Physique*, 1922, **17**, 416—441).— A résumé of work already published (A., 1910, ii, 771, 829; 1911, ii, 387). W. G.

**Equilibrium between Sulphur and Iodine in Solution.** M. AMADORI (*Gazzetta*, 1922, **52**, i, 387—394).—In view of the fact that the results of recent investigations indicate that the so-called compounds of sulphur with iodine described by various authors are merely mixtures of the two elements, the author has examined the solubility and cryoscopic relations of sulphur and iodine when present together. It is found that the separate solubilities of each of these elements in carbon disulphide, benzene, and bromoform are less than those which obtain in presence of the other element; in the first of these solvents both solubilities are increased by more than 100% by mixing the sulphur and iodine. The corresponding solubility curves of the mixtures in benzene and in carbon disulphide consist of two branches meeting in a point of double saturation.

Cryoscopic measurements of the mixtures in bromoform solution show that the depression of the freezing point of the solvent is somewhat less than that calculated from the molecular weights of the sulphur and iodine. No evidence is obtained of the existence of a solid compound of the two elements. T. H. P.

**The Crystallisation of Amorphous Tellurium.** A. DAMIE (*Compt. rend.*, 1922, **174**, 1548—1550).—From a study of t heats of reaction of different forms of tellurium with a mixtu of bromine and bromine water, Berthelot and Fabre have fou the relationship $Te_{cryst.} = Te_{amorph.} + 12{\cdot}096$ cal. (for 64 gram Previous work on the allotropy of tellurium did not confirm tl equation (cf. this vol., ii, 498), and the author has according repeated the work of Berthelot and Fabre, using, however, mixture of bromine and concentrated hydrochloric acid dilut with its own volume of water. His results do not confirm the of Berthelot and Fabre, but establish the equation $Te_{amorph.}$ $Te_{cryst.} + 2{\cdot}63$ cal., which is in accord with his work on the allotro of tellurium (*loc. cit.*). W. G.

**The Rectilinear Diameter of Nitrogen.** E. MATHI H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Ann. Physiq* 1922, **17**, 455—463). *A more detailed account of work alrea* published (A., 1915, ii, 143). W. G.

**Normal Density of [Chemically Pure] Nitrogen.** MOLES (*J. Chim. physique*, 1922, **19**, 283—289).—The results twenty-nine determinations of the density of pure nitrogen ha been systematically discussed, and from calculations, the weig of the litre of nitrogen at 0°, 760 mm., and 45° latitude is fou to be $L_N = 1{\cdot}2507 \pm 0{\cdot}0001$ grams. The measurements used a those of Rayleigh and Ramsay, Leduc, Gray, and Moles, in whi two entirely different methods were used, and the material w drawn from eight different sources. Under the conditions ( 760 mm., and $g = 980{\cdot}665$, the rounded value is $L_N = 1{\cdot}2507$ gran The actual value obtained from nitrogen obtained from sodiu *nitrite is $L_N = 1{\cdot}2506$ grams, a value which is almost identi* with the above-cited mean. This result is remarkable, since was obtained from volumetric determinations. J. F. S.

**The Synthesis of Ammonia by Collision with Slov moving Electrons.** E. BUCH ANDERSEN (*Z. Physik*, 1922, **1** 54—62).—A study of the action of a stream of electrons on t production of ammonia from mixtures of nitrogen and hydrog at low pressures. A current was passed between a glowing tungst wire and two platinum electrodes in an atmosphere of the t gases. The current was kept constant and the effect of variatio in the composition of the gas mixture and in the applied *E.M.* were investigated. The maximum rate of formation of ammor did not correspond with the stoicheiometric mixture, but wi mixtures containing a great excess of nitrogen. This result is agreement with the view that the first step in the production ammonia is the ionisation of the nitrogen molecule. Curves a given showing the velocity of formation of ammonia plotted agair the applied electromotive force. These curves show a series maxima at 22, 26, and 33 volts. No appreciable quantities ammonia were produced below an applied electromotive force

17·7 volts. This potential is identical with the ionisation potential of nitrogen (17·75 volts). It is, however, difficult to distinguish by direct measurement between the ionisation potentials of hydrogen and nitrogen. W. E. G.

**Oxidation of Nitric Oxide and the Recovery of Nitrogen Oxides from Mixtures with Air.** E. BRINER, S. NIEWIAZSKI, and J. WISWALD (*J. Chim. physique*, 1922, **19**, 290—309; *Helv. Chim. Acta*, 1922, **5**, 432).—The work which has been done on the commercial oxidation of nitric oxide and the recovery of oxides of nitrogen is reviewed and a number of points requiring further investigation are emphasised. Some of these points have been investigated by the authors. It is shown that the formation of nitrite by absorption of a gaseous system $NO—NO_2$ by alkali takes place according to the scheme proposed by Leblanc (*Z. Elektrochem.*, 1906, **12**, 541), based on the fact that nitrous anhydride exists in small concentrations, and this is in keeping with Raschig's experiments. Experiments on the oxidation of nitric oxide at low temperatures confirm the results of Lunge, Bodenstein, and Wourtzel, and show that the oxidation proceeds directly from nitric oxide to nitrogen tetroxide without the intermediate formation of nitrous anhydride. Comparative experiments made at ordinary temperatures, the temperature of carbon dioxide "snow" (−80°), and the temperature of liquid air (−190°) show that a low temperature is very favourable to the oxidation of oxides of nitrogen and to the recovery of the oxides. It follows from the experiments that cooling to a very low temperature will be the best means of effecting a complete recovery of the oxides of nitrogen from very dilute mixtures of these gases such as are obtained after passage through the electric arc, provided that the technical difficulties can be overcome, whilst without this low temperature very large oxidation chambers will be necessary.

J. F. S.

**Economic Realisation of Oxidation Reactions in Factories where Nitric Acid is Synthesised. Applications.** CAMILLE MATIGNON (*Bull. Soc. chim.*, 1922, [iv], **31**, 555—561).—The author proposes to use the dilute nitric acid such as is obtained at first in the fixation of atmospheric nitrogen or in the oxidation of ammonia, for chemical preparations in which it can be used as an oxidising agent, providing the reduction of the nitric acid does not proceed beyond the stage of nitric oxide. The oxides of nitrogen can be reconverted into nitric acid by atmospheric oxygen and again absorbed in the towers. In this way there is practically no loss of nitric acid and thus the expense of the oxidation process is very small. Suggested applications are the preparation of copper sulphate from copper by the combined action of sulphuric and nitric acids, and the preparation of oxalic acid from sugar or molasses by oxidation with nitric acid. This latter process was satisfactorily performed on a cargo of sugar damaged by sea water.

W. G.

**The Accessory Elements of the Dephosphoration Slags.** A. DEMOLON (*Compt. rend.*, 1922, **174**, 1703—1706).—Estimations have been made on a number of slags of the amounts of calcium soluble in solvents under definite conditions. The solvents used were: distilled water, 5% sugar solution, 2% phenol, a neutral solution of ammonium humate, cold solutions of ammonium chloride of different strengths, a saturated solution of carbon dioxide, and mineral acids. The amount of free calcium oxide in the slags was small, varying from 1% to 3%. In all the solvents the amount of calcium going into solution increased at first very rapidly with the time of shaking and then only very slowly over a long period of time. This is considered to be due to the presence of calcium silicates which react slowly with the solvents. The amounts of magnesium oxide present in the slags varied from 3% to 15% with an average of 8·90%. The amount of manganese found was fairly constant at about 4—5%, which was easily soluble in 2% citric acid. W. G.

**Magnetochemical Investigations of Constitutions in Mineral Chemistry. The Acids of Arsenic.** PAUL PASCAL (*Compt. rend.*, 1922, **174**, 1698—1700).—The results of measurements of the magnetic susceptibilities of a large number of arsenic compounds indicate that combined arsenic has two atomic susceptibilities according to the degree of saturation of its compounds. The results furnish further evidence in support of the rule that the logarithm of the atomic susceptibility of an element is a linear function of the atomic weight in each natural family. It is verified exactly for the group phosphorus, quinquevalent arsenic, and quinquevalent antimony and for the group tervalent arsenic, antimony, and bismuth. W. G.

**Reaction between Boron Nitride and Various Metallic Oxides with Production of Nitric Oxide.** U. SBORGI and A. G. NASINI (*Gazzetta*, 1922, **52**, i, 369—387).—Estimations have been made of the yields of nitric oxide obtained when air is passed over mixtures of boron nitride with various metallic oxides heated at different temperatures. Four samples of the nitride, prepared and stored in different ways, were employed. The yield of nitric oxide obtained varies greatly with these different samples and also with the nature of the admixed oxide. With the oxides $Fe_2O_3$, $Ni_2O_3$, $Co_2O_3$, $MnO_2$, $Mn_3O_4$ and $CuO$, yields as high as 72% are given, and the residue remaining after the reaction gives an increased yield of nitric oxide with a fresh quantity of boron nitride; this result is repeated four or five times, the yield increasing each time until the residue becomes converted into a compact mass.

T. H. P.

**Carbon and its Neighbours in the Periodic System.** ALFRED STOCK (*Z. angew. Chem.*, 1922, **35**, 341—343).—A discussion of the regularities occurring between the compounds of

the elements boron, carbon, nitrogen, and silicon. The greatest resemblances are found between the hydrides and their derivatives containing oxygen, nitrogen, or chlorine. In these compounds, carbon unites the chemical properties of its neighbours. It resembles boron in its tendency to form long chains of atoms, nitrogen in forming volatile compounds, and silicon and boron in giving rise to high-boiling derivatives. The property of combining equally readily with either electro-positive or electro-negative elements is shared to some extent by nitrogen and silicon. W. E. G.

**The Preparation of Carbon from Carbon Monoxide by means of a Catalyst.** J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 400—401).—An attempt to prepare pure carbon which, from the method of preparation, could not contain hydrogen or hydrocarbons, was unsuccessful. Carbon monoxide was passed over iron oxide at a temperature of about 450° and a good yield of carbon obtained. The resulting gas contained from 80—90% of carbon dioxide. The catalyst, however, was found to be fairly evenly distributed throughout the carbon, and prolonged attempts to extract it yielded a product the ash content of which was above 6%. H. J. E.

**The Rectilinear Diameter of Argon.** E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Ann. Physique*, 1922, **17**, 442—455).—A résumé of work already published (A., 1913, ii, 112, 478). W. G.

**The Analysis by Positive Rays of the Heavier Constituents of the Atmosphere; of the Gases in a Vessel in which Radium Chloride had been stored for Thirteen Years, and of Gases given off by Deflagrated Metals.** (Sir) J. J. THOMSON (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 290—299).—The positive ray method of analysis is applied to the solution of several problems. The residues from a thousand tons of liquid air have been examined for the presence of molecules heavier than krypton and xenon. Two new constituents of the atmosphere were found with molecular weights 163 and 260. The lighter of these is the more abundant, but the quantity in the air is very small compared with xenon. There is evidence that the lighter molecule carries two positive charges. No place in the periodic table can be found for a new element with this atomic weight, and it is possible that the two new lines are due to diatomic molecules of xenon and krypton.

The gases from 70 mg. of radium, stored in an evacuated vessel by (Sir) J. Dewar in 1909, have been analysed by the positive ray method. Helium and hydrogen were both present, but no neon or $H_3$ was found. In addition, a faint line, for which $m/e = 5$, seems to indicate a compound of helium with one atom of hydrogen. The analysis was also applied to gases which had stood over radium and to gases lit by deflagrating wires. The presence of doubly, triply, and quadruply charged atoms of oxygen and nitrogen, and

of doubly and triply charged atoms of carbon, was detected. . compound $m/e=10$ is believed to exist, consisting of an atom ‹ oxygen and four atoms of hydrogen. This invariably carries double charge. The deflagration of fine wires of tungsten, golc or copper by powerful electric currents did not yield any heliun although $H_3$ was detected. W. E. G.

**Constitution of Metallic Substances.** CHARLES A. KRAU (*J. Amer. Chem. Soc.*, 1922, **44**, 1216—1239).—A theoretica paper in which it is pointed out that the constitution of substance cannot be derived from their properties in a condensed state wit any considerable degree of accuracy. In order to determine th constitutions of metallic substances, it is necessary to study the: properties at low concentrations. At low concentrations, th elementary metals are salt-like substances, and it is suggested tha metallic compounds will exhibit salt-like properties in even a mor decided manner. In solutions of metallic compounds in liqui ammonia, the more electro-negative element functions as anior as follows from the fact that it is precipitated on the anode o electrolysis. All but the strongly electro-positive elements exhibi a negative as well as a positive valency. The normal anions c metallic elements form complex anions in the presence of th element in qnestion. These complex metallic compounds ar similar to the complex iodides and sulphides which have bee studied in aqueous solution. The property of forming comple anions is one common to many metallic as well as non-metalli elements. It is shown that the complex telluride-ion carries tw charges. In solution in ammonia, the complex anions $TeTe^{-}$ and $Te_3Te^{--}$ exist. It is inferred that the anions of the metal of the fifth group carry three charges, and those of the fourt four charges. Since it has been shown that selenium, telluriun bismuth, antimony, arsenic, tin, and lead form complex anion in ammonia solution, it may be inferred that other metal not soluble in ammonia form similar complex anions. Metalli compounds of this class are, therefore, virtually salts. Th multiplicity of compounds derivable from a given pair of metalli elements is accounted for on the hypothesis that in their compound the more electro-negative elements form complex anions, and thi view brings metallic compounds into line with the present con ceptions of atomic structure. The physical properties of metalli compounds are in keeping with the hypothesis that they posses a salt-like structure. It is pointed out that the energy effec accompanying the formation of metallic compounds is of th same order of magnitude as that accompanying the formation c salts, and as in the case of salts, the energy change is th greater the more electro-negative one element is with respect t the other. Electro-positive groups, such as the ammonium grouj are virtually metals, although their stability in the free state i not sufficient to permit their isolation in most instances. Th most stable groups possess sufficient stability to demonstrate thei

ıetallic properties in the free state. Such groups resemble elements ı their properties. The property of metallicity is not an atomic ne, it may be imparted to non-metallic elements by combination ʳith other non-metallic elements, and it is due to the presence of ncombined negative electrons. The electrons which impart ıetallic properties to an element are those to which the chemical eactions of this element with other elements are due. The eaction between strongly electro-positive and strongly electro-egative elements, or groups of elements, consists essentially in a ombination of the negative electrons of the electro-positive con-tituent with the atoms of the electro-negative constituent. In ıetal ammonia complexes of the type $Ca(NH_3)_6$, which are metallic ubstances, the negative electrons are not primarily concerned. 'he experimental data on which the foregoing conclusions are ased are to be published shortly. J. F. S.

**The Possible Existence of Metallic Compounds in the ·tate of Vapour.** A. EUCKEN and O. NEUMANN (*Z. Elektrochem.*, 922, **28**, 322—324).—Sodium amalgam was distilled at pressures etween 5 and 10 mm. of mercury, and the boiling point and orresponding composition of the vapour and liquid phases were etermined. The results indicate that, contrary to the suggestion f von Wartenberg (A., 1915, ii, 226), no appreciable amount of a ompound of sodium and mercury was formed in the state of apour at about 500°. J. S. G. T.

**Interaction of Sodium Chloride and Silica.** FRANCIS [ERBERT CLEWS and HUGH VERNON THOMPSON (T., 1922, **121**, 442—1448).

**Chlorites of Sodium and other Metals.** G. R. LEVI *Gazzetta*, 1922, **52**, i, 417—420; *Atti R. Accad. Lincei*, 1922, [v], **1**, i, 212—216; cf. this vol., i, 527).—The following new chlorites re described. *Sodium chlorite*, $NaClO_2,3H_2O$, prepared from ·arium chlorite and sodium sulphate, forms lustrous laminæ, and, ʳhen anhydrous, explodes on percussion. *Lithium chlorite*, similarly repared, forms anhydrous, deliquescent crystals and explodes on ercussion. *Calcium chlorite*, prepared from calcium peroxide and hlorine dioxide, explodes on percussion and decomposes com-letely in contact with a heated wire. *Strontium chlorite*, similarly btained, explodes on percussion, and in contact with a hot wire ecomposes with evolution of heat. *Thallous chlorite* explodes on ·ercussion and decomposes immediately at 70—80°. T. H. P.

**Oxidation and Reduction Reactions with Chlorites.** łIORGIO RENATO LEVI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 70—373; cf. preceding abstract).—At 180—200°, sodium chlorite ndergoes decomposition quantitatively in accordance with the quation $3NaClO_2=2NaClO_3+NaCl$. The action of ozone on he salt in aqueous solution yields chlorine dioxide, $2NaClO_2+$ $)_3+H_2O=2NaOH+O_2+2ClO_2$; if the dioxide is not carried away

by the ozone, it reacts either with the sodium hydroxide, $2NaOH+2ClO_2=NaClO_2+NaClO_3+H_2O$, or with hydrogen peroxide, if thi has been formed by the excess of ozone, $2NaOH+H_2O_2+2ClO_2=2NaClO_2+2H_2O+O_2$. In aqueous solution, sodium chlorit and nitrite react, with development of heat, forming the chlorid and nitrate, $2NaNO_2+NaClO_2=NaCl+2NaNO_3$. The reactio between a chlorite and a ferrocyanide is expressed by the equatio $4K_4Fe(CN)_6+NaClO_2+2H_2O=NaCl+4K_3Fe(CN)_6+4KOH$, an may be rendered complete either by gradual neutralisation of th alkali hydroxide by means of dilute sulphuric acid or by additio of a salt such as magnesium sulphate, magnesium hydroxide bein then deposited. With an iodide, sodium chlorite reacts with libera tion of iodine, $NaClO_2+4KI+2H_2O=4I+4KOH+NaCl$ (cf. Bray A., 1906, ii, 222, 223, 278), and here too the reaction may b carried to completion by addition of a substance, such as boric acid capable of neutralising the alkalinity; if the liquid is heated on water-bath and in an apparatus which prevents sublimation c the iodine, the reaction may be used for the estimation of a chlorit in presence of a chlorate, which does not liberate iodine under thes conditions. In neutral solution, chlorites do not act on alkal bromides, but in presence of sulphuric acid bromine is set free the behaviour towards bromates is similar. From acid solution of iodates and periodates no iodine is liberated, oxygenated com pounds of chlorine, formed by decomposition of the chlorous acid being obtained.

In neutral solution sodium chlorite reacts slowly with a sulphite thus: $2Na_2SO_3+NaClO_2=2Na_2SO_4+NaCl$; with solutions of fre sulphurous acid the corresponding reaction takes place immediately The reaction, $Na_2S_2O_3+2NaClO_2+H_2O=2NaCl+2NaHSO_4$, whicl occurs with development of heat, is complete only when either slight excess of chlorite is used or the liquid is kept neutral by mean of magnesium oxide; otherwise a little sulphurous acid is formed With thiocyanates, chlorites react principally according to th equation $2NaCNS+3NaClO_2+2H_2O=2NaHSO_4+2HCN+3NaCl$ slight excess of chlorite being required for the complete oxidatio of the sulphur of the thiocyanate to sulphuric acid. Chlorite oxidise hydrogen sulphide to sulphuric acid, and sodium format and oxalate to sodium hydrogen carbonate. T. H. P.

**Borates. VI. The System $(NH_4)_2O$—$B_2O_3$—$H_2O$ at 45° and at 90°.** UMBERTO SBORGI and LELIO FERRI (*Atti R. Accad Lincei*, 1922, [v], **31**, i, 324—329; cf. A., 1921, ii, 580).—In this system at 45° are found the 1 : 5 : 8- and the 1 : 2 : 4-compounds in addition to the 1 : 4 : 6-compound occurring at 60°; the first two compounds are able to exist unchanged in presence of pure water, but the 1 : 4 : 6-compound is found only in solutions con taining an excess of $(NH_4)_2O$ and having temperatures above that of the surrounding air. The same three compounds are formed also at 90°. T. H. P.

**The Electrolytic Preparation of Sodium Perborate.** KURT ARNDT and ERNST HANTGE (*Z. Elektrochem*, 1922, **28**, 263—273).—The conditions under which sodium perborate may be prepared electrolytically have been investigated. It is shown that this salt is most efficiently prepared from a solution of borax and sodium carbonate containing 120 grams of anhydrous sodium carbonate and 30 grams of borax per litre of solution. A small quantity of sodium chromate (0·5 gram per litre) and one drop of turkey red oil added to the electrolyte increases the efficiency, since this reduces the cathodic reduction to a minimum. A large anodic current density is requisite and to obtain this an anode of bright platinum is employed, whilst a water-cooled length of tin tubing serves as cathode. The most suitable current density lies between 10 and 20 amp./dcm.$^2$, and the most suitable temperature is 14—16°; above this temperature the yield of perborate is greatly reduced. During electrolysis, the bath loses carbon dioxide, and if this loss is not replaced the current yield becomes very poor owing to the large concentration of hydroxyl-ions. With an increasing concentration of the per-salt, the yield decreases during the electrolysis. The analysis of the hydrogen–oxygen gas mixture evolved during the electrolysis shows that a strong decrease in the anodic oxidation is responsible for the falling off of the yield. The merest trace of platinum salt in the electrolyte has a very bad effect on the yield, and the presence of iron in the sodium carbonate has a similar bad effect. Both substances decrease the anodic oxidation and increase the cathodic reduction. The addition of cyanide only partly eliminates the deleterious effect of the iron. The curve produced by plotting the current density against the anodic potential shows a sharp inflexion point at 1·47 volts. This potential is due to the concentration of a higher oxide of platinum, presumably $PtO_3$, which is formed as a solid solution in the anode material by the discharge of hydroxyl ions. It is likely that this higher oxide, in keeping with its potential and oxidising power, acts as an intermediate product in the formation of sodium perborate. J. F. S.

**Structure of Crystals of Lithium and some of its Compounds with Light Elements. II. Lithium Hydride.** J. M. BIJVOET and A. KARSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 26–30; cf. A. 1921, ii, 200).—Using the method of Debye and Scheerer, the authors have prepared and investigated the *X*-ray photographs of lithium hydride. The results show that lithium hydride crystallises in the regular system with four molecules in the elementary cell which has a side of length $a = 4{\cdot}10 \times 10^{-8}$ cm. The density of lithium hydride is calculated to be $0{\cdot}76 \pm 0{\cdot}01$. The structure is that of sodium chloride, with positive lithium ions and negative hydrogen ions. Systems of two-electron rings are round both the lithium and hydrogen nuclei with radii 0·05*a* and 0·6*a*, respectively, and the planes of which are normal to non-intersecting trigonal axes. J. F. S.

**Calcium-Ammonium.** E. BOTOLFSEN (*Bull. Soc. chim.*, 1922, [iv], **31** 561—567); cf. cf. Biltz and Hüttig, A., 1921, ii, 201).—Solid calcium-ammonium is formed within the temperature limits $-15°$ and $+30°$. The pasty state sometimes recorded in the literature is probably due to the presence of traces of sodium in the calcium used. The author confirms previous work on this compound (*loc. cit.*) in certain respects and finds that when it is heated in a vacuum at about 34° it decomposes explosively, the temperature depending slightly on the vacuum obtained. The products of this decomposition are the nitride and hydride of calcium and hydrogen. It is suggested that calcium is capable of forming a series of compounds with ammonia in much the same way as is iodine. W. G.

**The Transformation of Gypsum into Ammonium Sulphate.** C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1922, **175**, 33—35).—The authors obtained a 96% yield in the interaction of an industrial sample of gypsum with ammonium carbonate (cf. Neumann, A., 1921, ii, 587). The curves giving the velocity of the reaction show the existence of two distinct phases. During the first phase the velocity is slower than in the second phase. The presence of ammonium sulphate in the original solution causes a diminution in the velocity of the reaction, but in all cases equilibrium is complete at the end of two and a half hours. W. G.

**Magnesium-Cadmium Alloys.** LÉON GUILLET (*Rev. Met.*, 1922, **19**, 359—365).—The magnesium-cadmium alloys consist of a series of solid solutions and the compound CdMg, which is soluble in all proportions in either metal. Cadmium increases the hardness of magnesium, but the alloys are malleable up to a content of 55% Cd. With more than this they become brittle at ordinary temperatures, due to the formation of a new solid solution stable below 246° and consisting of the compound CdMg with excess of either magnesium or cadmium [cf. *J. Soc. Chem. Ind.*, 1922, 553A]. A. R. P.

**The Quaternary System Potassium Sulphate-Magnesium Sulphate-Ammonium Sulphate-Water.** ARNOLD WESTON (T., 1922, **121**, 1223—1237).

**Chemical and Electrochemical Behaviour of Salts of the Acids of Lead.** G. GRUBE (*Z. Elektrochem.*, 1922, **28**, 273—289).—Two new methods for the preparation of alkali salts of plumbic acid are described, the first of which consists in the anodic solution of a pure lead anode in a strong solution of alkali hydroxide by means of a direct current of high current density on which is superimposed an alternating current. In the second method, a solution of an alkali plumbite in concentrated alkali hydroxide is submitted to anodic oxidation at a platinum electrode. In both methods the alkali plumbates crystallise from the electrolyte in the pure condition during the electrolysis. The oxidation potentials of the processes

$Pb^{\cdot\cdot} + 2 \oplus \longrightarrow Pb^{\cdot\cdot\cdot\cdot}$ and $PbO_2'' + 2{\cdot}OH' + 2 \oplus \longrightarrow PbO_3'' + H_2O$ have been systematically investigated in alkaline solution and also the potential of lead in solutions of alkali plumbite has been measured. It is shown that the normal potential of lead against potassium plumbite in 8·42 $N$-potassium hydroxide at 18° is $\epsilon_h - 0{\cdot}613$ volt, whilst the normal potential of plumbite–plumbate in potassium hydroxide of the same concentration is $\epsilon_h + 0{\cdot}208$ volt. From these values the normal potential of lead against alkali plumbate solution is calculated to be $\epsilon_h - 0{\cdot}203$ volt. In all cases a decrease in the concentration of the alkali hydroxide displaces the potential toward more negative values. The nature of the plumbo-plumbates which separate from highly concentrated solutions of alkali plumbates and plumbites in alkali hydroxides has also been investigated, and it is shown that the composition of the deposit varies with the alkalinity of the solution in the sense that from solutions with a concentration of alkali hydroxide less than 4·9$N$, the compound $Pb_2O_3,3H_2O$ separates, whilst from solutions more concentrated than 6·9$N$, $Pb_3O_4$ separates. Hence it follows that $Pb_3O_4$ is to be regarded as the lead salt of ortho-plumbic acid, and that in very alkaline solutions of plumbates the anions of meta-plumbic acid, $PbO_3''$ and ortho-plumbic acid $PbO_4''''$, are both present. To ascertain whether the alkali plumbates are salts of the acid $H_2[Pb(OH)_6]$ or of $H_2PbO_3$, the author has investigated the dehydration of sodium plumbate, $Na_2PbO_3,3H_2O$. It is shown that on heating this salt the water is all expelled without decomposition of the salt, from which the conclusion is drawn that the three molecules of water are to be regarded as water of crystallisation and that sodium plumbate is a salt of metaplumbic acid. J. F. S.

**Effect of Grinding on the Apparent Density of Lead Oxides.** O. W. Brown, S. V. Cook, and J. C. Warner (*J. Physical Chem.*, 1922, **26**, 477—480).—The apparent density of heavy, crystalline lead oxide is diminished initially by grinding, the minimum value being attained by about ten hours' grinding in a pebble mill making 50 revolutions per minute. Thereafter, the apparent density increases, rapidly at first, to a constant value greater than the initial value. The initial decrease of apparent density is not shown by a light, amorphous lead oxide. J. S. G. T.

**Thermal Analysis of the System $Tl_2O$–$B_2O_3$.** G. Canneri and R. Morelli (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 109—111; cf. Buchtala, A., 1914, ii, 135).—The fusion diagram of this system exhibits three maxima corresponding with thallous metaborate, $TlBO_2$, m. p. about 474°; thallous pyroborate, $Tl_4B_2O_5$, m. p. about 434°; and normal thallous borate, $Tl_3BO_3$, m. p. 370° (decomp.). T. H. P.

**Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. II. Cementation of Copper by means of Chromo-manganese.** G. Sirovich and A. Cartoceti (*Gazzetta*, 1922, **52**, i, 436—442).—By means of

the arrangement previously used (this vol., ii, 68) experiments have been made on the cementation of copper by chromo-manganese containing 30·4% and 63·8% of chromium and manganese respectively. At 900°, the cementation is so intense that, in a few moments a layer of copper–manganese containing more than 20% of manganese is formed; as this alloy melts below 900°, the succeeding experiments were carried out at 800°. Although the iron of the ferro-manganese and the chromium of the chromo-manganese do not migrate to the copper, these metals evidently influence the migration of the manganese; the chromium having a greater effect than the iron. The mechanism of the process of cementation is discussed briefly. T. H. P.

**Action of Sulphur on Cuprous Chloride.** FREDERICK WILLIAM PINKARD and WILLIAM WARDLAW (T., 1922, **121**, 1300—1302.)

**The Structural Formula of Copper Sulphide.** W. GLUUD (*Ber.*, 1922, **55**, [*B*], 1760—1761; cf. this vol., ii, 446).—If hydrogen sulphide is passed into a 1·5% solution of copper sulphate in ammonia (10%) until only a faint blue colour remains, a variety of copper sulphide is precipitated which yields elementary sulphur on immediate oxidation by air, whereas after preservation for four or five hours it is oxidised to copper sulphate and thiosulphate. It is suggested that the formulæ Cu:S and $\begin{matrix}Cu\\Cu\end{matrix}\!\!>$S:S are to be assigned to the two modifications. This conception is in harmony with the known tendency of copper sulphide to pass into cuprous sulphide. The modification which yields free sulphur does not give potassium thiocyanate when treated with potassium cyanide; this reaction is shown strongly by the other variety. The difference is probably shown in the equations (i) $2CuS+10KCN=K_6Cu_2C_8N_8+2K_2S+C_2N_2$ and $C_2N_2+H_2O=HCN+HCNO$; (ii) $Cu_2S_2+8KCN=K_6Cu_2C_8N_8+K_2S_2$ and $K_2S_2+KCN=K_2S+KCNS$.
H. W.

**The Dissociation Pressures of Hydrated Double Sulphates. I. Hydrated Cupric Alkali Sulphates.** ROBERT MARTIN CAVEN and JOHN FERGUSON (T., 1922, **121**, 1406—1414).

**The Alloys of Cerium.** LÉON GUILLET (*Rev. Mét.*, 1922, **19**, 352—358).—The constitutional diagrams of alloys of cerium with iron, copper, aluminium, magnesium, bismuth, tin, and silicon are reproduced and discussed. Except in the case of iron in the iron-rich alloys, no solid solutions are formed with any of these metals, but a large number of definite compounds are known, some of which melt at a much higher temperature than either of the constituents; for example, $Bi_2Ce_3$ melts at 1,630° and $CeAl_2$ at 1,475°. There are two allotropic modifications of the compounds $CeFe_2$ and $CeAl_4$. As cerium increases the brittleness of metals with which it alloys, it is not suitable for use as a deoxidiser. A. R. P.

**Reactions of Sodium Hydroxide with Salts of Aluminium.** ÉDOUARD GROBET (*J. Chim. physique*, 1922, **19**, 331—335).—Making use of the thermal method of titration previously described (cf. this vol., ii, 578), it is shown that the addition of sodium hydroxide to dilute solutions of aluminium nitrate forms successively aluminium hydroxide, sodium metaluminate, and sodium ortho-aluminate. The addition of sodium hydroxide to dilute solutions of aluminium chloride, aluminium sulphate, and potash alum forms successively aluminium hydroxide, basic sodium aluminate, $Al(ONa)_3,Al(OH)_3$, and sodium ortho-aluminate. Sodium hydroxide added to concentrated solutions of aluminium chloride, nitrate, or sulphate produces a basic salt of the type $AlX_3,Al(OH)_3$, which is followed by the hydroxide, meta-aluminate and ortho-aluminate. Concentrated solutions of potash alum yield under the same treatment a basic salt, $Al_2(SO_4)_3,2Al(OH)_3$, aluminium hydroxide, a basic aluminate, $Al(ONa)_3,Al(OH)_3$, and the ortho-aluminate.

J. F. S.

**Crystal Structures of the Hexa-ammoniates of the Nickel Haloids.** RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1239—1245).—The crystal structure of the complex compounds of the type $NiX_2,6NH_3$, formed when ammonia is added to solutions of nickel chloride, bromide, and iodide respectively, has been examined by means of *X*-ray photographs. It is shown that the arrangement of the atoms in the crystals of these substances is such that the salts are strictly isomorphous with those of ammonium platinichloride (this vol., ii, 214). The dimensions of the unit cell and the values of the variable parameters defining the positions of the nitrogen atoms in the chloride and iodide have been estimated. The following values are recorded: $NiCl_2,6NH_3$, side of unit cell 10·09 Å.U.; $NiBr_2,6NH_3$, length of side of unit cell, 10·48 Å.U.; $NiI_2,6NH_3$, length of side of unit cell 11·01 Å.U. In each case there are four molecules in the unit cell. The nickel atoms occupy the position of platinum, and the halogen atoms those of nitrogen in the ammonium platinichloride crystal.

J. F. S.

**Composition and Crystal Structure of Nickel Nitrate Hexammoniate.** RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1260—1266).—From analyses, *X*-ray spectrum measurements, and considerations of space group arrangements, it is shown that neither of the formulæ $Ni(NO_3)_2,4NH_3,H_2O$, or $Ni(NO_3)_2,4NH_3,2H_2O$ is correct for the pale blue isotropic octahedra which are obtained when an excess of a concentrated solution of ammonia is added to an aqueous solution of nickel nitrate. The true formula is $Ni(NO_3)_2,6NH_3$. A study of the Laue photographs of these crystals by the generally applicable methods which use the theory of space groups indicates that they have a structure similar to that of the corresponding complex haloids (preceding abstract), in which the nitrate groups replace the halogen groups, and in which the ammonia groups are related to the nickel atoms in exactly the same

way in both compounds. The position of the atoms of the nitrate groups cannot be determined with great accuracy. Both the symmetry characteristics and the diffraction data permit the same kind of displacement of the nitrate nitrogen atoms as is experienced by the sulphur atoms in pyrites. The unit cube contains four molecules and the length of its side is 10·96 Å.U. J. F. S.

**Solubility. VI. Solubility of Ammoniates.** FRITZ EPHRAIM and PAUL MOSIMANN (*Ber.*, 1922, **55**, [*B*], 1608—1619; cf. A., 1921, i, 508).—In a previous communication it has been pointed out that the similarity between dissolved substance and solvent has an important influence on solubility and that salts can achieve this similarity with water as solvent by the formation of hydrates or solvates. An experimental examination of this hypothesis has now been attempted by investigating the solubility in water of salts in which the formation of hydrates is rendered difficult. This can be achieved by occupying the co-ordination positions which would eventually be filled by water with other neutral groups, for example, ammonia. A relationship might therefore be expected between the solubility of a series of ammoniates such as $[Ni(NH_3)_6]X_2$ and their ammonia tension. A difficulty, however, arises, since many of these salts are decomposed by water and their solubility has therefore been determined in aqueous ammonia solution, $d^{22}$ 0·950, to which half its volume of alcohol (96%) has been added. With the hexamminenickelo-salts there is a parallelism between solubility and ammonia tension in the series iodide ⟶ bromide ⟶ chloride ⟶ thiocyanate, whilst the perchlorate and formate occupy the expected position in the series; on the other hand, in the series tetrathionate ⟶ thiosulphate ⟶ sulphide ⟶ chloride ⟶ nitrate ⟶ chlorate, the solubility increases with decreasing ammonia tension. In general, therefore, there is no parallel between ammonia tension and solubility, at any rate in the cases of the ammoniates of the salts containing oxygen. The experiments have been extended to the ammines of copper and cadmium salts; in the oxygen-free salts, a relationship is observed between ammonia tension and solubility, but it is doubtful if this is more than accidental, since the solubility is so greatly affected by the nature of the medium. The ammines of cobalt and chromium are more suitable, since they dissolve in water to a reasonable extent and are not decomposed thereby. The two series $[Co(NH_3)_6]X_3$ and $[Cr(NH_3)_6]X_3$ are so similar in their general properties that it would be expected to find the solubilities of the salts falling in the same order. This is actually the case to a great extent, but the parallelism is not complete. Particularly in the case of the cobalt compounds, the salts fall into two distinct groups, in which the solubilities are of widely differing orders of magnitude, the boundary lying between the perchlorate and oxalate. Possibly the two portions comprise the true salts and pseudo-salts respectively.

The following compounds have not been described previously:

*hexamminecobaltic naphthalene-β-sulphonate* $[Co(NH_3)_6][C_{10}H_7SO_3]_3$, pale yellow, microscopic needles; *hexamminecobaltic picrate*, $[Co(NH_3)_6]$ $[O{\cdot}C_6H_2(NO_2)_2]_3$, microscopic needles; *hexamminechromic dichromate*, $[Cr(NH_3)_6]_2[Cr_2O_7]_3$, lustrous, hexagonal needles; *hexamminechromic picrate*, small, matted needles; *hexamminechromic naphthalene-β-sulphonate*, pale yellow, microscopic needles; *hexamminechromic perchlorate*, pale yellow needles; *hexamminechromic chlorate*, slender, pale yellow needles. The hexammineohromi-salts resemble the alkaloids in giving *precipitates* with the following reagents: potassium mercuric iodide (slender, yellow needles), potassium bismuth iodide (microcrystalline, reddish-brown powder), sodium cobaltinitrite (very small, reddish-brown crystals). The solubilities of the following hexamminecobalti-salts (gram.-mol. per litre) in water at 9° have been estimated: chloride (0·20), bromide (0·040), iodide (0·015), nitrate (0·033), sulphate (0·015), perchlorate (0·013), chlorate (0·215), chromate (0·00055), dichromate (0·00029), oxalate (0·00069), phosphate (0·00055), naphthalene-β-sulphonate (0·00059), picrate (0·00042). The hexamminechromi-salts have the following solubilities at 17·5°: chloride (0·42), bromide (0·118), iodide (0·043), nitrate (0·072), dichromate (0·005), sulphate (0·046), phosphate (0·0032), oxalate (0·00084), picrate (0·00037), naphthalene-β-sulphonate (0·00069), chlorate (0·062), perchlorate (0·0199). H. W.

**Hydrous Oxides. III.** Harry B. Weiser (*J. Physical Chem.*, 1922, **26**, 401—434).—In continuation of previous work (A., 1920, ii, 760), the author has studied the properties of various hydrous chromic oxides prepared under different conditions. The results indicate that no definite hydrates of chromic oxide are formed by precipitating a chromic salt with alkali. The evidence that Guignet's green is a definite hydrate is inconclusive. Hydrous chromic oxide freshly precipitated in the cold is readily soluble in acids, but becomes insoluble on keeping or heating. Between the two extremes of solubility an indefinite number of hydrous oxides exists. By precipitating hydrous chromic oxides at temperatures from 0° to 225°, substances ranging in colour from greyish-blue to bright green have been prepared. Positively charged colloidal hydrous chromic oxide may be prepared by peptising the hydrous oxide with chromic chloride, and by hydrolysis of the chloride or nitrate, but not of the acetate. The negatively charged colloid is prepared by peptising the hydrous oxide with sodium or potassium hydroxides. The properties of the respective colloidal suspensions are discussed, more especially the precipitating and peptising action of alkali salts. J. S. G. T.

**Precipitation from Uranyl Nitrate by means of Sodium Hydroxide. Radioactivity of the Precipitate.** Pierre Jolibois and Robert Bossuet (*Compt. rend.*, 1922, **174**, 1625—1628).—When sodium hydroxide is added to a dilute aqueous solution of uranyl nitrate precipitation only commences when an equimolecular

amount of sodium hydroxide has been added. From this stage up to the addition of two molecules a precipitate is obtained, and if this is filtered off and the filtrate is boiled, a further precipitate is deposited. Either precipitate contains 1·5% or more of sodium hydroxide which is not removed by washing. If more than two molecules of alkali are added precipitation is complete and the precipitate contains still higher percentages of alkali. Radioactivity measurements on the different precipitates show that the intensity of radiation is proportional to the amount of radium present. The first precipitate which is formed contains a very important proportion of the uranium-*X*, the oxide of which is apparently less basic than that of uranium. W. G.

**Solubility in the Solid State of Bismuth and Cadmium in Lead.** CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 162—164).—By means of the method devised by Plato (A., 1906, ii, 521; 1907, ii, 239), the author has investigated the fusion diagrams of the systems Pb–Bi and Pb–Cd. The results obtained give for the solid solubility of lead in bismuth the value 4% and for that of bismuth the value 34%. For lead in cadmium or cadmium in lead the solid solubility is practically zero; in this system the specific thermal conductivity varies linearly with the composition. T. H. P.

## Mineralogical Chemistry.

**A New Occurrence of Ilsemannite.** CHAS. W. COOK (*Amer. J. Sci.*, 1922, [v], **4**, 50—52).—A large number of molybdenum deposits were examined, but ilsemannite was detected only at Ouray in Utah (A. 1917, ii, 491) and near Gilson in California. At the latter locality, molybdenite occurs with pyrites in aplite, and is often completely altered to yellow molybdenite. A brown tarnish suggests a first stage in the alteration to molybdenum dioxide; and a later stage to a mixture of dioxide and trioxide is suggested by the presence of a blue material which is insoluble in water. Ilsemannite, the blue soluble material, is perhaps a hydrated compound of dioxide and trioxide. L. J. S.

**Chemical and Spectrochemical Study of Spanish Bismuth Minerals.** S. PIÑA DE RÚBIES and F. GILA ESTEBAN (*Anal. Fis. Quim.*, 1921, **19**, 347—386; cf. Piña de Rúbies, A., 1921, i. 267).—A description with chemical analyses and spectrographical data of bismuth minerals occurring in Spain. A series of minerals is described having a chemical composition varying between bismuthospherite, $(BiO)_2CO_3$, and bismuthite, $BiO{\cdot}CO_3{\cdot}Bi(OH)_2$.

Another class of minerals includes oruetite, $Bi_8TeS_4$, and antimoniferous bismuthine. Oruetite and similar minerals are probably eutectic mixtures of bismuth, tetradymite, $Bi_2Te_3$, and bismuthine, $Bi_2S_3$. The carbonate minerals of the first series may be derived from the oruetite minerals. Native bismuth, scheelite, and molybdenite are also described. G. W. R.

**Ardennite from Ceres, in the Ala Valley (Piedmont).** FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 147—151).—This mineral occurs, intimately associated with piedmontite and mixed with various other species, in aggregates of colophony-brown, vitreous fibres or rods, often twisted or bent. The crystals exhibit marked pleochroism and the other optical characters observed with the ardennite found in the Belgian Ardennes, and have the following percentage composition :

| $SiO_2$. | $As_2O_5$. | $P_2O_5$. | $V_2O_5$. | $Al_2O_3$. | $Fe_2O_3$. | CuO. | CaO. | SrO. | BaO. |
|---|---|---|---|---|---|---|---|---|---|
| 29·53 | 10·30 | 0·12 | 0·25 | 22·40 | 3·11 | 0·75 | 5·61 | trace | trace |

| MnO. | NiO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$—. | $H_2O$+. | Total. |
|---|---|---|---|---|---|---|---|
| 18·76 | 0·04 | 4·03 | 0·07 | 0·12 | 0·12 | 5·42 | 100·63 |

These results correspond well with the formula

$$10SiO_2,(As,V,P)_2O_5,5(Al,Fe)_2O_3,10(Mn,Mg,Ca,Cu)O,6H_2O.$$

The mineral is almost pure arsenioardennite, the proportion of vanadioardennite being very small. T. H. P.

**The Melting of Potash Felspar.** G. W. MOREY and N. L. BOWEN (*Amer. J. Sci*, 1922, **4**, 1—21).—A pure synthetic orthoclase was prepared by crystallising glass of the composition $KAlSi_3O_8$ in a bomb containing water vapour, and this material was used for determining the melting point of the pure substance. The temperature usually given for the melting point, determined on natural crystals, is 1200°. It was found that orthoclase has no true melting point. When kept for a week at 1200°, it forms a glass which, under the microscope, is seen to have a cross-lined structure. At higher temperatures, the structure becomes more distinct and develops into typical leucite crystals. The temperature range of incongruent melting, in which leucite crystals are in equilibrium with liquid, is 1170—1530°. Three natural potash felspars showed the same behaviour, namely, microcline from N. Carolina, sanidine from Laacher See, and adularia from St. Gotthard, but in these the upper limit was lowered somewhat by the foreign matter present. It follows that orthoclase must be considered as a binary compound in the leucite–silica ($KAlSi_2O_6$–$SiO_2$) system. The general form of the diagram of this system is shown, but only a few points on it have yet been accurately determined. The incongruent melting of orthoclase is of particular importance for the theory of rock formation. It shows that leucite can form from a liquid containing an adequate amount of silica, or even excess, for orthoclase formation and that a mass

may have leucite as early crystals (phenocrysts) together witl free silica as late crystals (ground-mass). The regular behaviou of leucite in breaking up into orthoclase and nephelite suggest that the early separation of leucite may afford a key to the origi of many nephelitic rocks as well as of leucite rocks. E. H. R.

**Tridymite from the Euganean Hills, Italy.** EDOARD BILLOWS (*Mem. Accad. Lincei*, 1922, [v], **13**, 506—524).—A detailed crystallographic description of tridymite from the trachyt of Zovon in the Euganean Hills near Padua. The crystals ar cloudy and now consist of an aggregate of quartz. L. J. S.

## Analytical Chemistry.

**Behaviour of Platinum on Strong Ignition.** D. BALAREF (*Chem. Ztg.*, 1922, **46**, 573).—On heating either new or carefull cleaned old platinum crucibles in a blast flame or over a powerfu Teclu burner, a fairly constant loss in weight of 0·6 mg. per hou was noticed, whilst the side of the crucible nearest the blast wa considerably brighter than that more remote. No experiment were made, however, to find an explanation of the loss.

A. R. P.

**Heavy Liquids for the Separation of Minerals.** ENRIC CLERICI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 116—118; cf. A 1911, ii, 257).—The following three liquids, useful for the mechanica separation of minerals of different densities, are colourless an may be diluted and recovered: Aqueous barium bromomercurat solution $d^{11}$ 3·11, $d^{18}$ 3·14. Saturated aqueous thallium format solution, $d^{10}$ 3·31, $d^{20}$ 3·40, $d^{90}$ 4·10. Aqueous solution of thalliur formate and thallium malonate in equal proportions, $d^{10}$ 4·0( $d^{50}$ 4·70, $d^{\text{about } 100}$ above 5. Thallium formate, melting at 95° to highly mobile liquid, may also be used, and a mixture of thalliur formate and malonate in equal amounts melts below 95° an has $d$ above 5. Fused thallium formate has $d$ below 5, but i dissolves powdered thallium carbonate, giving a liquid with above 5. T. H. P.

**A New Physico-chemical Method of Volumetric Analysi applied to some Problems of Inorganic Chemistry.** PAU DUTOIT and ED. GROBET (*J. Chim. physique*, 1922, **19**, 324—327).— A method is described by which solutions of acids may be titrate

with bases using a thermometer graduated in 1/100° as indicator. The solution to be titrated is placed in a small Dewar vessel, which stands in a somewhat larger Dewar vessel, a mechanical stirrer is placed in the solution, and the alkali is added at regular intervals in amounts which cause the temperature to increase by not more than 0·02°. The burette is surrounded by asbestos paper and the stopcock is operated by a long pair of pincers. The number of c.c. of alkali added are plotted as abscissæ and the temperature after each addition as ordinate, and the points joined. It is found that the end-point is marked by a decided change of direction in the curve. Not only is this point fixed by the curve, but all other points at which a change in the nature of the reaction occurs are fixed. Thus with sulphuric acid the points corresponding with the completion of the formation of the hydrogen sulphate and the normal sulphate are both accurately shown. In the titration of phosphoric acid with sodium hydroxide the points where the formation of $NaH_2PO_4$, $Na_2HPO_4$, and $Na_3PO_4$, respectively, is complete are well marked. In the titration of normal sodium phosphate with nitric acid, the points where the formation of $Na_2HPO_4$, $NaH_2PO_4$, and $H_3PO_4$ is complete are clearly marked. The titration of the nitrates of zinc, lead, and magnesium by this method indicates the completion of the formation of definite basic salts, and in the case of the two first-named metals, of zincates and plumbites, respectively. Titration of salts of cobalt, copper, and nickel with ammonia in the same way indicates the formation of the various ammonia complexes. This method yields identical results with those obtained by electrometric and electroconductivity titrations and in addition it also indicates the formation of derivatives which these methods do not. J. F. S.

**Simple Method of Electrometric Titration in Acidimetry and Alkalimetry.** PAUL FRANCIS SHARP and F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1922, **44**, 1193—1196).—The object of the work described is the preparation of a number of constant and reproducible electrodes which are electrometrically equivalent to hydrogen electrodes dipping in solutions of various known hydrogen-ion concentrations. Such electrodes are extremely useful in cases where it is necessary to titrate a solution of an acid to an end-point which shall have a definite hydrogen-ion concentration. In such a case, the half cell containing a hydrogen electrode and the solution being titrated is connected with the electrode which has the same potential difference as the hydrogen electrode will have when the titration is completed. A solution of alkali is then run into the acid until a galvanometer indicates that the total cell, comparison electrode|sat. KCl|titration liquid|$H_2$Pt, has a zero *E.M.F.* The following are the comparison electrodes together with the potential against a normal calomel electrode and the equivalent hydrogen-ion concentration:

| | | | |
|---|---|---|---|
| HgPb— | | | |
| (12—12·5%) | 0·52 c.c. KI in 100 c.c. solution ‖; | *E.M.F.* | 0·5195 = $10^{-4}N$-H |
| ,, | 2·90 c.c. KI ,, 100 ,, ‖ | ,, | 0·5609 = $10^{-4.7}N$-H |
| ,, | 6·14 c.c. KI ,, 100 ,, ‖ | ,, | 0·5786 = $10^{-5}N$-H |
| ,, | 67·50 c.c. KI, in 100 ,, ‖ | ,, | 0·6378 = $10^{-6}N$-H |
| HgCd— | | | |
| (12—12·5%) | 100 c.c. $CdSO_4$ + 0·2 c.c.KI ‖ | ,, | 0·6967 = $10^{-7}N$-H |
| ,, | 10 c.c.$CdSO_4$ + 10 c.c.KI in 100 c.c. sol. ‖ | *E.M.F.* | 0·7560 = $10^{-8}N$-I |
| ,, | 100 c.c. $CdSO_4$ + 26·40 c.c. KI ‖ | *E.M.F.* | 0·8151 = $10^{-9}N$-H |
| ,, | 2c.c. $CdSO_4$ + 48·7c.c. KI in 100c.c. sol. ‖ | *E.M.F.* | 0·8743 = $10^{-10}N$-I |

The number of c.c. of potassium iodide and cadmium sulphate refer respectively, to 2·0*N*- and 0·5*N*-solutions, respectively (cf. Pinkho A., 1920, ii, 121). J. F. S.

**The Use of Potassium Ferrocyanide in Potentiometri Titrations. II. The Potentiometric Titration of Zinc** I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 425—437).—Th possibility of this titration has been established for some tim (Koninck and Prost, A., 1896, ii, 675), but no worker has yet state the degree of accuracy with which determinations may be mad (cf. Bichowsky, A., 1917, ii, 219). The author recommends th use of a solution of potassium ferrocyanide, the concentration o which is 1/40 mol., to this is added 1 gram per litre of potassiun ferricyanide. The standardisation of the zinc solution for th control experiments, which is described in detail, is a matter o difficulty; in previous work sufficient attention does not seem t have been directed to accuracy in this respect. The titration i *best carried out at 70°, as at this temperature the reaction i* quicker and the change in potential which denotes the end-poin is greater. As the results obtained in neutral solution are too low *1—2* c.c. of 4*N*-sulphuric acid should be added. Excess, however should be avoided, otherwise the precipitate of potassium zin ferrocyanide is partly dissolved and the change in potential at th end-point diminished. In such a solution 0·2 mg. of zinc may b determined within 1%. In presence of potassium sulphate at 70% and of ammonium sulphate at ordinary temperatures, results ar obtained which are 0·5% too high; the latter salt at 70° has th reverse effect, which is also given by ammonium chloride. Th titration may be carried out speedily and accurately in the invers direction. H. J. E.

**Estimation of Chlorine in Organic Compounds.** J. KLIMON (*Chem. Ztg.*, 1922, **46**, 521—522).—Attempts were made to esti mate chlorine in organic compounds by boiling the latter witl alcoholic potassium hydroxide solution under a reflux apparatu and titrating the excess of alkali subsequently with standard acid Acetylene dichloride, monochlorohydrin, monochloroacetone, di chloroacetone, α-chloronaphthalene, dichloronaphthalene, borny chloride, and pinene hydrochloride yielded either low or untrust worthy results; trichloroethane, acetylene tetrachloride, and α-di bromohydrin yielded high results, whilst monochloroacetic acic gave a correct result. W. P. S.

**Estimation of Free Chlorine and Hypochlorous Acid in Concentrated Salt Solutions.** M. C. Taylor and C. A. Gammal (*J. Ind. Eng. Chem.*, 1922, **14**, 632—635).—The estimation of free chlorine and hypochlorous acid in concentrated salt solutions, which may contain either sodium hypochlorite or hydrochloric acid, is usually carried out by estimations of total "available" chlorine, and of free chlorine by an aeration process. The latter, however, is inaccurate owing to decomposition of hypochlorous acid or of hypochlorite during aeration. It is now shown that the rate of the removal of the free chlorine is a linear function of the amount present at any moment, whilst when all free chlorine has been removed the rate of removal varies as the square of the amount of hypochlorous acid present. The curves obtained by plotting the rate of removal of chlorine against the total amount removed as measured by absorption in potassium iodide solution and titration with thiosulphate will therefore be two distinct lines having a point of intersection, the abscissa of which is the free chlorine initially present as such. To obtain the amount of chlorine initially present as hypochlorous acid and hydrochloric acid, the increase in acidity after aeration is determined by means of potassium iodide–iodate solution in terms of thiosulphate solution, and this is equal to the actual loss of chlorine during aeration due to such reactions as $HOCl \rightarrow HCl + O$. G. F. M.

**Estimation of the Chlorometric Degree of Bleaching Chlorides.** J. Royer (*Ann. Falsif.*, 1922, **15**, 146—148).—For the estimation of available chlorine in bleaching solutions the method of Poncius is recommended as being rapid and exact. It consists in titrating the solution with standard potassium iodide in the presence of sodium hydrogen carbonate. The first reaction consists in the oxidation of the iodide to iodate, but as soon as the free chlorine has been used up the next drop of iodide solution reacts with the iodate with the liberation of free iodine, which is indicated by starch paste. W. G.

**Electrometric Titrations with Silver Nitrate. Estimation of Chlorides, Bromides and Iodides, and of Iodides in the Presence of Chlorides and Bromides.** I. M. Kolthoff (*Z. anal. Chem.*, 1922, **61**, 229—240).—In most cases the solubility of the silver compound indicates whether the end-point of a titration with silver nitrate solution may be ascertained electrometrically. The method is trustworthy for chlorides, iodides, and bromides, even in very low concentration, and iodides may be titrated in ammoniacal solution in the presence of chlorides and bromides. Certain complex salts, such as ferrocyanides, pyrophosphates, etc., cannot be estimated by the method, although with ferricyanides and thiocyanates the results obtained are accurate. The method may also be used for the estimation of cyanides, chromates, oxalates, tartrates, succinates, and salicylates. W. P. S.

**Estimation of Minute Amounts of Gaseous Oxygen and its Application to Respiratory Air.** HOWARD M. SHEAFF (*J. Biol. Chem.*, 1922, **52**, 35—50).—The method is intended mainly for use in following the oxygen consumption of plant and animal tissue under different conditions. By means of the apparatus, which is described and illustrated in the original, it is stated that oxygen can be estimated in amounts as small as $1 \times 10^{-7}$ gram. The method depends on the conversion of the oxygen, in the presence of nitric oxide and sodium hydroxide, into sodium nitrite, and the estimation of the latter colorimetrically by means of sulphanilic acid and α-naphthylamine. E. S.

**The Oxygen-absorption and Concentration of Pyrogallol Solutions used in Gas Analysis.** FRITZ HOFFMANN (*Z. angew. Chem.*, 1922, **35**, 325—328).—The absorptive powers of solutions of pyrogallol and potassium hydroxide of all proportions are tabulated in a Gibbs triangular diagram for the ternary system pyrogallol, potassium hydroxide, and water. A line of maximum absorptions was found to correspond with mixtures containing pyrogallol and potassium hydroxide in the proportions 3 to 2. The field to one side of the line, corresponding with a smaller proportion of the latter, falls sharply in power of absorption. The optimum proportion is given as pyrogallol 20 parts, potassium hydroxide 20 parts, and water 60 parts. H. M.

**Rapid Estimation of Sulphur. I.** LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 204—206).—The method here described depends on the fact that, if a compound containing sulphur is heated with powdered iron in absence of air, the sulphur in the residual mass is liberated completely as hydrogen sulphide on subsequent treatment with hydrochloric acid. This gas is absorbed by zinc acetate solution and the sulphide thus formed estimated by titration with iodine solution. Tests made on flowers of sulphur and on copper, lead, barium, and cobalt sulphates gave excellent results. The method is applicable also to the estimation of sulphur in organic compounds, but the latter must previously be heated with copper oxide or lead chromate in a porcelain crucible, or, if the organic compound is volatile, in a narrow hard glass tube, in which it is covered with a deep layer of the oxidising material [cf. *J. Soc. Chem. Ind.*, 1922, 614A]. T. H. P.

**The Kleemann Modification of the Kjeldhal Process.** FRANTIŠEK SKUTIL (*Chem. Listy*, 1922, **16**, 173—177).—The various methods of estimating the nitrogen of foodstuffs and manures, using modifications of the Kjeldhal process, are reviewed, and the advantages of the Kleemann modification (*Z. angew. Chem.*, 1921, **34**, 625) pointed out. Results obtained by a modification of this method are found to be in satisfactory agreement with those obtained by the standard analytical method used in Czecho-Slovakia. This method differs from that of Kleemann in that, after the addition of mercury, 30% of hydrogen peroxide is added, and then the

concentrated sulphuric acid, slowly, and with cooling. After some time, the contents of the flask are heated until a deep coloration appears. Finally, anhydrous potassium sulphate is added, and the process completed. R. T.

**The Estimation of the Total Non-protein Nitrogen of Serum. Comparative Study of Trichloroacetic and Metaphosphoric Acids as Protein Precipitants.** PAUL CRISTOL (*Bull. Soc. Chim. Biol.*, 1922, 4, 267—271).—Higher values are obtained for total non-protein nitrogen when proteins are precipitated by means of metaphosphoric acid than when trichloroacetic acid is used for this purpose. This is due to the partial hydrolysis of the proteins by the former reagent. E. S.

**The Estimation of Non-protein Nitrogen in Blood.** ERIC PONDER. (*Biochem. J.*, 1922, **16**, 368—369).—Blood (0·2 c.c.) is added to water (1 c.c.) and the pipette used is washed out twice, each time with a further 0·2 c.c. of water. The protein is precipitated with 0·2 c.c. of a 10% solution of sodium tungstate and 0·2 c.c. of 2/3*N*-sulphuric acid as in Folin's method for the preparation of blood filtrates. 0·5 C.c. of this filtrate is boiled very gently with 0·2 c.c. of a digestion mixture diluted 1 in 4. The digestion mixture consists of 50 c.c. of a 5% copper sulphate solution, 100 c.c. of 85% phosphoric acid, and 300 c.c. of pure sulphuric acid. After boiling for two minutes, water is added to make the volume 3·5 c.c., and the solution is directly nesslerised and compared with a standard solution of ammonium sulphate. W. O. K.

**Detection and Estimation of Nitrate Nitrogen in Urine and Serum.** O. NOLTE (*Z. anal. Chem.*, 1922, **61**, 278—282).—The presence of nitrates may be detected by means of the diphenylamine reaction or by the less sensitive ferrous sulphate reaction; the diphenylamine reaction, however, is obtained with oxidising substances other than nitrates. For the estimation of nitrates in urine, the Schlösing-Grandeau gasometric method appears to be the most trustworthy, but the nitric oxide content of the volume of gas obtained must be estimated subsequently. W. P. S.

**Analytical Determination of Oxides of Nitrogen in Gas Mixtures.** CHARLES L. BURDICK (*J. Ind. Eng. Chem.*, 1922, **14**, 308—310).—Mixtures of nitrogen peroxide and nitric oxide are absorbed in dilute alkali in accordance with the equations $3NO_2 + 2NaOH = 2NaNO_3 + NO + H_2O$ and $NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O$. If previous to absorption there is a development of mist in consequence of cooling, the nitrogen peroxide present in the hot gas will be partly converted into nitric acid and nitric oxide. An absorption apparatus must therefore provide for the measurement of nitric oxide passing through the alkali unabsorbed. The absorption bulb in the apparatus described is a tube containing a number of glass bells with side perforations placed vertically above one another and with the inlet tube passing down through

their central axes. This is filled with a known volume of $N/10$ alkali hydroxide free from carbonate diluted as required. The gas passes through this into an aspirator, in which it is treated with hydrogen peroxide, absorbed in excess of alkali hydroxide, and estimated as usual. The solution in the absorption bulb is titrated with $N/10$-sulphuric acid, using a few drops of a solution of methyl-red in $N/100$-alkali hydroxide as indicator. To the neutralised solution a known excess of permanganate with 5 c.c. of sulphuric acid are added, the solution is left for a few minutes a slight excess of ferrous sulphate added, and the excess titrated back. If there is no acid mist present and if $A$ c.c. of alkali and $P$ c.c. of permanganate are neutralised in the absorber, it will be seen that of this $(3A+P)/2$ c.c of alkali hydroxide have been neutralised by nitrogen peroxide and the total alkali hydroxide $-(3A+P)/2$ c.c. by nitric oxide.

If nitric acid mist is present, it is absorbed as nitrate in the bulb and is measured by the excess of alkali hydroxide neutralised over the nitrite formed, whilst the nitrite formed contains twice the quantity of nitrogen present as nitrogen peroxide. If more than 5% of excess oxygen is present in the gas mixture, a correction for oxidation during the passage of the gas through the sampling tube should be applied. C. I.

**A Possible Source of Error in the Bell-Doisy Method for the Estimation of Phosphates in Blood Plasma.** W. DENIS and L. VON MEYSENBUG (*J. Biol. Chem.*, 1922, **52**, 1—3).—The method of Bell and Doisy (A., 1920, ii, 769) for the estimation of phosphates in blood gives accurate results when applied to serum, but low values are obtained when plasma is used. Serum should therefore be used for this estimation ; if, however, plasma is used, the accuracy may be increased by restricting the amount of anti-coagulant and increasing the quantities of molybdic acid and quinol. E. S.

**Microchemical Investigation of Arsenic.** ARNALDO PIUTTI and ENRICO BOGGIO-LERA (*Mem. Accad. Lincei*, 1922, [v], **13**, 475—479).—In the detection of arsenic in very small proportions, good results are obtained by using a reagent composed of 1 c.c. of 3% ammonium molybdate solution, 10 c.c. of 3·4% ammonium nitrate solution, and 39 c.c. of 40% nitric acid solution. With liquids containing 0·02—0·004 mg. of arsenic per c.c., this reagent is used directly, but for lower concentrations of arsenic the reagent is diluted five times with 40% nitric acid. A drop of the arsenic solution yields characteristic microscopic crystals when evaporated with a drop of the reagent. As little as 0·00005 mg. of arsenic is detectable in this way. T. H. P.

**Estimation of Arsenic Acid.** L. ROSENTHALER (*Z. anal. Chem.*, 1922, **61**, 222—229).—Diffused light does not interfere in the iodometric estimation of arsenic acid, but atmospheric oxygen

reacts with the hydriodic acid formed, yielding further quantities of free iodine. This may be prevented by adding 5 grams of sodium hydrogen carbonate before the potassium iodide is introduced. The titration solution should contain at least 16% of hydrochloric acid or 33·3% of sulphuric acid. When sulphuric acid is used, the following procedure should be adopted. The iodate solution is treated with concentrated sulphuric acid in quantity sufficient to make the concentration of the latter 33·3%, the mixture is cooled, and 5 grams of sodium hydrogen carbonate are added in small quantities at a time ; concentrated potassium iodide solution is now added, and the iodine is titrated with *N*/10-thiosulphate solution. A precipitate which forms on the addition of the iodide consists chiefly of arsenic tri-iodide, and should be dissolved by adding a small quantity of water before the titration is commenced.

W. P. S.

**Iodometric Estimation of Arsenic and Antimony Sulphides.** FERDINAND NIKOLAI (*Z. anal. Chem.*, 1922, **61**, 257—272).—Arsenites and the corresponding antimony salts may be estimated volumetrically by adding their solutions to an excess of standard iodine solution containing dilute acetic acid and sodium acetate and then titrating the excess of iodine with thiosulphate solution. Arsenic trisulphide, or antimony trisulphide, may be titrated by dissolving it in sodium hydroxide solution and adding this solution to iodine solution containing acetic acid and sodium acetate, with subsequent titration of the excess of iodine. The alkaline solution of the sulphide is oxidised readily by atmospheric oxygen, but this may be prevented, or the rate of oxidation retarded to a considerable extent, by the addition of a small quantity of gelatin.

W. P. S.

**Tests of an Iodine Pentoxide Indicator for Carbon Monoxide.** S. H. KATZ and J. J. BLOOMFIELD (*J. Ind. Eng. Chem.*, 1922, **14**, 304—306).—The "Hoolamite" carbon monoxide indicator consists of a glass tube containing granulated pumice impregnated with 1 part of iodine pentoxide to 5 parts of fuming sulphuric acid (60% $SO_3$). The gas is drawn through cotton-wool filters and a tube of activated charcoal into a rubber hand bulb and discharged through the tube containing the pumice. The colour produced on the latter is matched with a series of permanent colours in a sealed glass tube. A series of tests with a large number of observers showed that by this instrument a minimum concentration of 0·07% of carbon monoxide can be detected, and that a rough quantitative estimation of higher concentrations can be made. In the absence of the activated charcoal most hydrocarbons, hydrogen sulphide, and hydrogen chloride interfere; methane, chlorine, carbon dioxide, sulphur dioxide, and some other gases do not. The "Hoolamite" tube may be used for six to eight estimations, after which it deteriorates.

C. I.

**The Direct Estimation of Small Quantities of Radium by the Penetrating Rays.** B. SZILARD (*Compt. rend.*, 1922, **174**, 1695—1698).—The electrometer previously described (*ibid.*, 1922, **174**, 1618) has been modified so as to provide a transportable instrument working without either a high tension battery or a projection mirror. By means of it rapid measurements can be made of the penetrating rays. The sensitiveness of the instrument corresponds with $10^{-4}$ *U.E.S.* W. G.

**Ash-alkalinity (of Foodstuffs).** B. PFYL. (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 313—339).—To utilise the titration values of the ash of foodstuffs as indications of their composition, it is necessary to choose the values, to be determined in such a way that they are definite and as independent as possible of chance circumstances, and to employ simple and unexceptionable methods for determining them. The chemical processes taking place during the incineration of foodstuffs have to be considered more closely than has been done in the past, and the necessity for avoiding loss of mineral acids and for the conversion of the whole of the phosphorus into tribasic phosphate must be kept in view. In many cases this can only be attained by the addition of a measured quantity of alkali before incineration. The most useful values to be determined are (*a*) the intrinsic alkalinity, (*b*) the methyl-orange alkalinity, and (*c*) the total phosphate of the ash. The first may be defined as the excess, expressed in milli-equivalents, of the kations $Na^{\cdot}$, $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, which remains after combination with the anions $PO_4'''$, $SO_4''$, $Cl'$ for $O''$, and the weakly acid anions $CO_3''$, $SiO_3''$, $BO_2'$, $MnO_3''$, $MnO_4''$, $AlO_2''$. If such excess does not exist, the difference is expressed as "intrinsic acidity." (*b*) is the excess, expressed in milli-equivalents, of the same four kations which remains after combination with the anions $H_2PO_4'$, $SO_4''$, and $Cl'$ for $O''$, and the above enumerated weakly acid anions. The absence of such excess is indicated as methyl-orange acidity. (*c*) The total phosphates is expressed in milli-equivalents of $PO_4'''$. These three values can be obtained by titration against methyl-orange, followed by a titration against phenolphthalein. Full details of simple methods of carrying out the above determinations are given; these are the result of many years of experience, and are founded on sound scientific principles. Modifications necessary in special cases and precautions and corrections to be applied where special accuracy is needed are also indicated. The above three values are usually calculated to 100 grams of dry food-stuff or 1 litre of liquid, but occasionally to 1 gram of ash or 1 gram of ash soluble in hydrochloric acid. In cases of adulteration, one or other of these values is affected. Methods proposed by others for the determination and presentation of ash-alkalinity are criticised.

H. C. R.

**Atkinson's Process for the Estimation of Potassium in the Presence of Sodium, Magnesium, Sulphates, and Phosphates.** S. J. WATSON (*Analyst*, 1922, **47**, 285—288).—The

process is considered unsatisfactory because the compensating errors necessary to overcome the loss due to the solution of some potassium perchlorate do not occur to an extent sufficient to balance this loss, and the quantity of methyl alcohol and perchloric acid used is too large to make the process economical. Keeping the contents of the beaker at the boiling point for an hour, whilst perhaps necessary to ensure complete solution of undesirable substances, must also favour the solution of potassium perchlorate itself. H. C. R.

**The Estimation of Calcium in Blood.** ARTHUR ROBERT LING and JOHN HERBERT BUSHILL (*Biochem. J.*, 1922, **16**, 403—406).—Two to 5 c.c. of blood are incinerated in a platinum dish, treated with 1·5 c.c. of concentrated hydrochloric acid, and washed into a special centrifuge tube. After adjusting the reaction, the calcium is precipitated with oxalic acid and ammonium oxalate. The calcium oxalate is centrifuged and washed, sulphuric acid is added, and the oxalic acid titrated with permanganate.

W. O. K.

**A Colorimetric Method for the Estimation of Small Amounts of Magnesium.** F. S. HAMMETT and E. T. ADAMS (*J. Biol. Chem.*, 1922, **52**, 211—215).—The method is designed for application to urine, blood, and tissue extracts and is a modification of Kramer and Tisdall's method (A., 1921, ii, 595). The precipitate of ammonium magnesium phosphate obtained in the latter method is dissolved in 0·01*N*-hydrochloric acid and the phosphorus estimated colorimetrically by Bell and Doisy's method (A., 1920, ii, 769). The value for magnesium is then calculated from this result. E. S.

**Volumetric Estimation of Lead Peroxide in Miniums. Practical Modification of Diehl's Method.** A. BONIS (*Ann. Falsif.*, 1922, **15**, 157—159).—The following modified procedure for Diehl's method of estimating lead peroxide in samples of minium is advocated. Half a gram of the sample is macerated with 2·5 c.c. of nitric acid (*d* 1·080) and the mixture is washed into a conical flask with 25 c.c. of a saturated solution of sodium acetate. To this is added 10 c.c. of a 12% solution of potassium iodide in saturated sodium acetate, and the whole is well shaken, and the iodine liberated is titrated with *N*/10-thiosulphate solution. If the sample of minium contains iron oxide, instead of titrating the free iodine an excess of standard thiosulphate is added and the whole is made up to 100 c.c. with the saturated sodium acetate solution. After filtering, an aliquot portion of the filtrate is titrated back with *N*/10-iodine solution. W. G.

**Rapid Electro-analysis.** A. KLING and A. LASSIEUR (*Ann. Chim. Analyt.*, 1922, **4**, 171—177).—For the rapid electrolytic deposition of copper or zinc a silver cathode is recommended

together with an anode of platinum alloyed with iridium or rhodium. The silver cathode is readily cleaned without loss in weight by immersion in a cold solution of 10 grams of trichloroacetic acid in 50 c.c. of strong ammonia and 50 c.c. of water. Copper is deposited from a sulphate solution acidified with nitric acid and containing 5 grams of sodium metaphosphate if iron is present. Zinc is deposited from a solution containing sodium acetate and 5 c.c. of acetic acid per 100 c.c., together with 10 c.c. of a saturated solution of sodium fluoride if iron is present; large quantities of iron should, however, be separated. Lead may be deposited on the anode as peroxide from a solution containing 15 c.c. of nitric acid per 100 c.c., or as metal on the cathode by electrolysing at 70° with 5 amperes a solution containing less than 0·4 gram of lead and 3 c.c. of nitric acid (*d* 1·3), 2·5 grams of crystallised gallic acid, and 5 c.c. of 95% alcohol in 100 c.c. total bulk. Antimony may be electrolysed from a solution containing 80 c.c. of sodium sulphide solution (*d* 1·14), 60 c.c. of water, and 5 grams of potassium cyanide by a current of 5 amperes at 60—70°, or from a boiling solution containing 20 c.c. of hydrochloric acid and 4 grams of hydroxylamine hydrochloride in 130 c.c. of water. The latter solution, with the addition of 10 grams of ammonium oxalate, may be used for the deposition of tin. The above methods are adapted to the rapid analysis of brasses, bronzes, and white metals [cf. *J. Soc. Chem. Ind.*, 1922, 551A]. A. R. P.

**Iodometric Estimation of Copper in the Presence of Iron.** A. Wöber (*Z. angew. Chem.*, 1922, **35**, 336—337).—Solutions containing copper salts in the presence of ferrous iron always contain a small amount of cuprous ions. These cannot be oxidised by nitric acid or hydrogen peroxide in ammoniacal solution, as the small amount of nitrites formed interferes with the subsequent titration. The solution is therefore made ammoniacal and treated with a current of air at 70°, whereby all the copper dissolves as cupric salt and the iron is precipitated as ferric hydroxide, which is collected, re-dissolved and re-precipitated to recover the adsorbed copper. The combined filtrate is boiled to expel ammonia, acidified, treated with potassium iodide, and titrated as usual [cf. *J. Soc. Chem. Ind.*, 1922, 545A]. A. R. P.

**Separation of Aluminium from Iron by means of o-Phenetidine.** K. Chalupny and K. Breisch (*Z. angew. Chem.*, 1922, **35**, 233—234).—The solution containing the iron and aluminium salts is slightly acidified with hydrochloric acid and treated with a current of hydrogen sulphide for ten minutes; carbon dioxide is then passed through the solution until all excess of hydrogen sulphide has been expelled. These operations are carried out in a flask closed with a cork and provided with inlet and outlet tubes. Ammonium carbonate is then added until a precipitate forms, the latter is dissolved by the addition of dilute hydrochloric acid, and an excess of 5% alcoholic phenetidine

solution is added. The flask is closed, the contents are heated at 80°, and the precipitate is then collected, washed with hot, dilute ammonium nitrate solution, ignited, and weighed as aluminum oxide. If copper and other metals are present with the iron and aluminium, the copper must be separated electrolytically, the iron and aluminium then precipitated as basic acetates, the latter dissolved in dilute hydrochloric acid, and the solution used for the separation of the iron and aluminium as described. It is essential that the iron should be present in the ferrous state; ferric salts yield a precipitate with phenetidine solution. W. P. S.

**Gravimetric Analysis. XXV. Estimation of Manganese.** L. W. WINKLER (*Z. angew. Chem.*, 1922, **35**, 234—235; cf. A., 1921, ii, 656).—The manganese is precipitated as manganese ammonium phosphate, the method being that described previously (*loc. cit.*) for the estimation of cadmium. Small corrections are applied to the weight of precipitate obtained; for instance, 1 mg. is deducted when the precipitate weighs 0·2 to 0·3 gram. The presence of potassium chloride does not interfere, but sodium chloride must not be present. W. P. S.

**Oxidation of Manganese to Permanganate in Alkaline Solution.** J. HESLINGA (*Chem. Weekblad*, 1922, **19**, 274).—Manganese in ores and alloys is readily detected by heating the solution with potassium hydroxide and excess of copper sulphate (which acts as a catalyst), and adding a few drops of a mixture of bromine water and potassium hydroxide; the violet coloration due to permanganate develops at once. 0·005 Mg. of manganese may be detected. The reaction is not suitable for quantitative estimation, since it is only complete where very small quantities of manganese are present; also the presence of iron affects the colour, probably by formation of potassium ferrate.

The catalytic action of the copper oxide is probably due to its tendency to form easily dissociated oxygen compounds, and its tendency to form compounds with manganese hydroxide. More copper than manganese must be present, otherwise the catalyst remains in this combination. S. I. L.

**The Adsorption of Iron by Precipitates of Manganese Dioxide.** MAX GELOSO (*Compt. rend.*, 1922, **174**, 1629—1631; cf. Nicolardot, Geloso and Réglade, A., 1920, ii, 334).—When manganese is precipitated as its dioxide by the addition of ammonium persulphate to an acid solution of manganese sulphate containing some iron salt, the amount of iron adsorbed by the precipitate varies directly with the amounts of iron and manganese present in the solution and inversely with the acidity. The presence of ammonium sulphate has no effect. The iron adsorbed is mostly in the form of hydroxide. W. G.

**Estimation of Chromium in Steels.** LUIGI LOSANA and ENRICO CAROZZI (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 197—200).—Gravimetric methods for estimating chromium in steel give good

results but are too tedious for industrial use, and colorimetric methods are not to be recommended. Provided that attention is directed to various points, satisfactory results are obtained by Stead's method, in which the chromium is oxidised by means of nitric acid and by permanganate to chromic acid and this is treated with ferrous sulphate, the excess of the latter being titrated with permanganate. Modifications are suggested which render the ammonium persulphate method more rapid and exact [cf. *J. Soc. Chem. Ind.*, 1922, 594A]. T. H. P.

**New Qualitative Test for Uranium.** HAROLD D. BUELL (*J. Ind. Eng. Chem.*, 1922, **14**, 593).—Uranium may be detected in slags or ores by preparing a nitric acid solution of the material, too great an excess of acid being avoided, and adding an excess of granulated zinc. When the reaction with the acid has subsided, a yellow deposit will appear on the zinc if uranium is present. Gold, platinum, thorium, lead, tungsten, titanium, chromium, mercury, and copper do not interfere with the test. Iron and vanadium only interfere if present in large quantities, and in that case the spent liquid is removed, and the zinc and the deposit are again treated with nitric acid. The deposit dissolves, but reappears when the acid is again exhausted, and vanadium and iron remain in solution. As regards the delicacy of the test, in a solution of pure uranyl nitrate it was possible to detect 0·88 mg. of uranium per c.c. The test is not applicable in presence of sulphuric or hydrochloric acids. The yellow deposit is apparently the hydrated trioxide, $UO_3,2H_2O$. G. F. M.

**Colorimetric Estimation of Vanadium in Steel.** A. KROPF (*Z. angew. Chem.*, 1922, **35**, 366—367).—The steel is dissolved in a mixture of nine parts of sulphuric and one part of phosphoric acid to prevent separation of tungstic acid. The solution is oxidised first with nitric acid, then with ammonium persulphate to destroy carbonaceous matter, and the colour produced by hydrogen peroxide in this solution is matched with that produced by a known amount of vanadium pentoxide added to a solution containing approximately equal amounts of chromium, nickel, and hydrogen peroxide [cf. *J. Soc. Chem. Ind.*, 1922, 594A.] A. R. P.

**Rapid Detection of Bismuth in Urine and in Saliva.** DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1922, **61**, 321—326).—For the detection in urine of small proportions of bismuth, which is administered in the form of sodium or potassium bismuthotartrate (cf. Sazerac and Levaditi, this vol., i, 89) in cases of syphilis, good results are obtained by means of stannous chloride solution, prepared by dissolving 10 grams of the crystallised salt in 10 c.c. of concentrated hydrochloric acid and heating the liquid with a few pieces of tin on a water-bath until it becomes almost clear (cf. Vanino and Treubert, A., 1898, ii, 461). Ten c.c. of the urine are treated with 2 c.c. of this reagent and then with 5 c.c.

of 20% sodium hydroxide solution, and the whole is shaken. If the urine contains salts of bismuth, these undergo reduction to the metal, which is deposited with the precipitated calcium and magnesium phosphates and gradually colours these brown or black; in some cases, also, the supernatant liquid becomes brown owing to dissolution of part of the bismuth in the colloidal condition. Saliva may be tested similarly. That the dark precipitate actually contains bismuth may be shown by conversion of a little of it into the vivid red bismuth rubidium iodide, $BiI_3,2RbI,2\cdot5H_2O$, and microscopic examination of this.

Nylander's test for dextrose (A., 1884, 1433) may be used inversely as a test for bismuth, but is not so sensitive as that given above. T. H. P.

**Estimation of Minute Quantities of Methane.** Ernst Murmann (*Oesterr. Chem.-Ztg.*, 1922, **25**, 90).—The estimation of small quantities of methane, involving the absorption of the carbon dioxide derived therefrom in baryta solution, has hitherto required two or more absorption flasks to ensure the complete removal of carbon dioxide from the gases owing to the short time in which the bubbles are in contact with the liquid. One ordinary Erlenmeyer flask only is sufficient, however, if the gases are led into the baryta solution through a capillary tube and 0·5—1·0 c.c. of 1% gelatin solution is added to the liquid so as to make a foam on the surface which increases the duration of contact of the gases and the absorbent solution to at least thirty seconds, and renders absorption thereby complete. The capillary may conveniently be fixed into the flask through the straight arm of a T-piece fitted into a rubber stopper, and the connexion made gas-tight with a piece of rubber tube. The artifice may also be useful for other cases where complete absorption of a gas by a liquid is required.

G. F. M.

**The Estimation of Benzene in Gases.** E. Berl (*Z. angew. Chem.*, 1922, **35**, 332).—The benzene is absorbed by carbon, which is then heated at 100—120° in a current of steam (in a salt-bath). A small amount of benzene remains behind, and therefore a test is made with carbon containing benzene to control the results. The burette filled with water in which the benzene is collected is provided with an overflow in such a manner that the benzene remains in the burette. This method is simpler and better than that by which the benzene is washed out of the gases with light petroleum. H. M.

**Some New Colour Reactions of Cholesterol.** Louis Kahlenberg (*J. Biol. Chem.*, 1922, **52**, 217—225).—Cholesterol dissolves in arsenic trichloride to a pink solution changing to cherry-red; *iso*cholesterol yields a cobalt blue solution changing through violet, purple, and dark red to dark green; phytosterol, however, dissolves to a colourless solution. The colours are discharged by the addition of solvents such as benzene, toluene, and

chloroform. The colour reactions are also obtained with hot solutions of arsenious oxide in concentrated hydrochloric acid, but are not so permanent as with the anhydrous chloride. Coloured solutions, which are not, however, sufficiently characteristic to be used for distinguishing between the sterols, are also obtained with certain other acid chlorides. E. S.

**Analytical Observations on the True Blood-sugar Value in Normal and Pathological Individuals.** WILHELM STEPP (*Arch. expt. Path. Pharm.*, 1922, **90**, 105—128).—A series of analyses of blood-sugar was carried out in the following way: the proteins were removed with phosphotungstic acid and the sugar estimated by a reduction method (that of Bertrand or Laquenne); a further amount of the filtrate was freed from phosphotungstic acid with lead acetate, the excess of lead removed, and the solution concentrated; the concentrated fluid was analysed for sugar by a reduction method, by fermentation, and polarimetrically.

The values obtained by the reduction methods on the untreated filtrate were 20% to 100% higher than those obtained on the filtrate after concentration; the difference was greatest in cases where there was nitrogen retention, and was proved to be not due to loss of sugar in the process of analysis.

The agreement between the results obtained by the three methods on the concentrated filtrate was, on the whole, good, the polarimetric and fermentation methods giving especially close agreement. It is suggested that nitrogenous reducing substances are carried down in the process of removing the excess of phosphotungstic acid, and that the lower values obtained after this treatment represent the true concentration of sugar in the blood.

C. R. H.

**The Inversion of Sucrose in the Alkaline Copper Solution.** E. CANALS (*Bull. Soc. chim.*, 1922, [iv], **31**, 583—588).—Results indicate that sucrose is slowly hydrolysed during the estimation of reducing sugars in its presence by means of some form of Fehling's solution. The actual amount of sucrose hydrolysed increases with the concentration of the sucrose, with the time of heating, and with the temperature at which the liquid is kept. It is essential therefore to make a blank estimation, and it is advisable to heat by immersion in a water-bath. W. G.

**Estimation of Humus by Oxidation with Chromic Acid.** A. GEHRING (*Z. anal. Chem.*, 1922, **61**, 273—278).—The soil is first treated with dilute sulphuric acid in a flask through which a current of air free from carbon dioxide is passed. When all carbon dioxide produced by the decomposition of carbonates has been expelled, potassium dichromate is added to the flask and the mixture is heated; the carbon dioxide and other gases resulting from the oxidation of the organic matter are passed through a combustion tube containing copper oxide and lead chromate, and the carbon dioxide is then absorbed in potash bulbs. W. P. S.

**Oxidation with Mixtures of Sulphuric Acid and Chromates.** L. J. SIMON (*Compt. rend.*, 1922, **174**, 1706—1708).—For the wet combustion of organic compounds by means of chromic acid, the most satisfactory results are obtaiued by the use of concentrated sulphuric acid and silver chromate, using about 15 c.c. of the acid and 12 grams of the chromate for about 0·1 gram of substance. This oxidising mixture may be used for the combustion of acetates or acetyl derivatives, theoretical results being obtained.
W. G.

**Analysis of Acetic Anhydride.** C. EDWARD SAGE (*Perf. Essent. Oil Rec.*, 1922, **13**, 172).—In the method described by Reclaire (this vol., ii, 532) for the estimation of acetic anhydride, the phenolphthalein used as indicator seems with certain samples to be peculiarly insensitive. The actual cause of this is obscure, but the peculiarity seems to run parallel with the development of the iodoform reaction when the sample in question is tested with sodium hydroxide and iodine. The unknown impurity giving this reaction may be traced back to the original acetic acid from which the anhydride was prepared, and it seems to be associated with faults in odour which sometimes develop in products prepared from the anhydride, for example, aspirin, or synthetic "acetyl" perfumes. The insensitiveness of phenolphthalein above mentioned may be overcome, and a sharp end-point obtained if the titration is made by adding an excess of *N*/2-hydroxide, keeping for some time without heating until hydrolysis is complete, then adding a known quantity of *N*/2-acid and finishing off the titration with more *N*/2-hydroxide. By this procedure errors due to heating under reflnx will also be eliminated. G. F. M.

**Estimation of Fatty Acids (and Cholesterol) in Small Amounts of Blood Plasma.** W. R. BLOOR, K. F. PELKAN, and D. M. ALLEN (*J. Biol. Chem.*, 1922, **52**, 191—205).—Bloor's method (A., 1914, ii, 392) for the estimation of fatty acids in blood probably gives incorrect results owing to the different nephelometric values which the various fatty acids and cholesterol possess (cf. Csonka, A., 1918, ii, 277). To overcome this two modifications are suggested: (1) the separation of cholesterol from the fatty acids and the separate estimation of the two fractions thus obtained (cf. A., 1916, ii, 275), (2) the use of a standard, consisting of 60% oleic and 40% palmitic acid, which melts at approximately the same temperature as the mixture obtained from blood. Using these modifications, the results are accurate to within 5%. E. S.

**Estimation of Small Amounts of Lactic Acid.** S. W. CLAUSEN (*J. Biol. Chem.*, 1922, **52**, 263—280).—The method of Fürth and Charnass is slightly modified. Lactic acid is decomposed either by acid permanganate at 95° or by 50% sulphuric acid at 140°, the aldehyde produced being swept into excess of sodium hydrogen sulphite. The excess of the sulphite is removed by addition of iodine, the end-point being adjusted to a definite blue

to starch. Saturated sodium hydrogen carbonate is then ad until the blue coloration is just discharged, and the sulphite of aldehyde bisulphite compound titrated with standard iodine, end-point being determined by a blank control. The errors wh arise when the method is applied to blood or urine may be reduc but not entirely eliminated, by first extracting the lactic a from the protein-free filtrate by ether, using a special extract apparatus. E. S

**Detection and Estimation of Oxalic Acid and its Use Standardising Iodine and Silver Solutions.** L. Rosenthal (*Z. anal. Chem.*, 1922, **61**, 219—222).—Iodine is liberated wl potassium iodate solution is heated with the addition of a sm quantity of oxalic acid; the reaction may be obtained with 3r of oxalic acid and permits of the detection of the latter in presence of tartaric and malic acids which reduce the iodate m more slowly. Oxalic acid and oxalates may be estimated by heat their dilute sulphuric acid solution with an excess of stand iodate solution until all free iodine has been expelled, cooling mixture, and titrating the excess of iodate with thiosulphate solut after the addition of potassium iodide. It is proposed to sodium oxalate for the standardisation of iodine solutions and silver nitrate solutions; in the latter case, a known quantity the oxalate is treated with a slight excess of silver nitrate soluti the mixture diluted to a definite volume, filtered, and the exc of silver titrated in an aliquot portion of the filtrate with tl cyanate solution. W. P. S

**Oxidation of Oxalic Acid in the Absence of other Aci** J. C. Witt. (*J. Physical Chem.*, 1922, **26**, 435—446).—It is shc that oxalic acid may be titrated with potassium permangan without the addition of any other acid, the oxalic acid function both as reducing agent and acid. The end-point is marked the appearance of turbidity followed by a slight permanent p cipitate and is affected by the temperature of titration, the c centration, and the presence of electrolytes. When a solution an oxalate is titrated in the presence of sulphuric acid, the coll precipitating power of the sulphate-ion is effective in the prese of a fairly high concentration of the hydrogen-ion, and hence quantity of sulphuric acid required is much greater than theoretical value. J. S. G. T

**Standard Method for the Estimation of Soap in Wo** British Research Association for the Woollen and Wors Industries (*Trans. Text. Inst.*, 1922, **13**, 143—149).—Traces soap left on a woollen fabric may cause serious disturbances dyeing, and consequently may require estimation. It is shc that extraction at the boiling point with neutral absolute alcol in a glass apparatus with ground-in joints, satisfactorily remo the soaps and free fatty acids from the material. J. C. W

**Olive Oils and the Villavecchia Reaction.** JEAN PRAX (*Ann. Falsif.*, 1922, **15**, 159—161).—It has been shown previously (*ibid.*, 1921, **14**, 270) that certain olive oils, particularly Tunisian, give a red coloration with Villavecchia's reagent, similar to that given by an olive oil adulterated with sesamé oil. This abnormal reaction is not obtained if such an oil is shaken with its own volume of 90% alcohol containing 10% of ammonia and the alcohol and ammonia then evaporated on a water-bath before applying the test. It is now shown that it is as a result of the action of the ammonia that these abnormal oils no longer give the red coloration with the Villavecchia reagent. W. G.

**The Orcinol Reaction with Furfuraldehyde. Application to the Colorimetric Estimation of Small Quantities of Furfuraldehyde.** PAUL FLEURY and GABRIEL POIROT (*Bull. Soc. Chim. Biol.*, 1922, **4**, 252—266).—For the estimation, 1 c.c. of the furfuraldehyde solution and 5 c.c. of a hydrochloric acid reagent (*d.* 1·19 and containing about 60 mg. of ferric chloride per litre) are added successively to 4 c.c. of an orcinol reagent (1 gram of orcinol in 1600 c.c. of glacial acetic acid). The mixture is then heated for one minute on a water-bath, left for half an hour at the ordinary temperature, and the blue coloration compared with that produced in a standard solution treated simultaneously in the same manner. The standard solution contains 0·1 mg. of furfuraldehyde per c.c.; that to be estimated should contain between 0·01 and 0·30 mg. E. S.

**A Cause of Error in the Application of the Colour Test for Acetone.** ANTONIO TROISE (*Ann. Chim. Analyt.*, 1922, **4**, 177—178).—On testing a sample of urine for acetone by means of ammonia and sodium nitroprusside in acetic acid (Lieben's reaction) the characteristic violet colour was obtained, although the distillate did not give the reaction. The cause of the colour was found to be the presence of *istycine* (1·8 *dihydroxyanthraquinone*) which had been taken medicinally. A. R. P.

**Differentiation and Estimation of Saponins.** L. KOFLER (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 278—287).—The usual methods of investigation do not suffice to arrive at the identity of a saponin when it is not available in the pure state. The author makes use of the foaming power in addition to the hæmolytic action of saponins. The "foam number" is obtained by shaking up 10 c.c. of each of a series of solutions of different concentrations in test-tubes 16 mm. internal width for fifteen seconds and allowing them to remain for fifteen minutes. The foam number is given by the dilution in that tube in which the foam stands 1 cm. high. The hæmolytic index is determined in the usual way, the details of which are specified. If the hæmolytic index is divided by the foam number, a quotient is obtained which is independent of the state of purity of the saponin. This quotient has a characteristic value for each of the six different saponins investigated, varying

from zero in the case of glycyrrhizin to 10 in the case of Merck's digitonin. By this means saponins separated from artificia lemonades by Brunner's method (*ibid.*, 1902, **5**, 1197; 1908, **16** 165; 1912, **23**, 566; 1914, **27**, 192) can be readily identified anc quantitatively estimated by comparing the hæmolytic index anc foam value obtained with those tabulated for the saponin ir question. It would be possible to specify a maximum value fo: the "poison/foam" quotient which should not be exceeded by the saponins used in food-stuffs. The figure 1·0 or 0·5 is suggested

H. C. R.

**The Defecation of Blood for the Estimation of Carbamide** AL. IONESCU (*Bul. Soc. Chim. Romania*, 1922, **4**, 13—17).—Th defecating agent recommended consists of a saturated aqueou solution of sodium chloride to which has been added 10% of glacia acetic acid. To the serum an equal volume of this reagent i added and the mixture is heated to boiling and filtered. Th filtrate is made slightly alkaline with sodium hydroxide and th carbamide estimated in an aliquot portion by the hypobromit method.

W. G.

**The Testing of Foodstuffs for Vitamins.** J. C. DRUMMONI and A. F. WATSON (*Analyst*, 1922, **47**, 235—246).—Details are give of the method of carrying out physiological tests on rats for th presence of the three vitamins in foodstuffs. Young healthy rat of not more than 50 grams body weight are fed on a ration of puri fied foodstuffs from which all traces of the vitamin to be tested fo have been removed. These rations are specified for each of th three vitamins. When the rats have shown no further incremen of weight for fourteen days, the substance to be tested is adminis tered in a daily ration of known weight. The method has bee used to show that samples of butter vary very considerably in th amount of vitamin they contain.

The amount of vitamin-*B* in milk depends entirely on the food o the cow. The monkey is the best animal for testing for vitamin-*C* but the guinea pig is generally used. Testing is rendered mor difficult by the fact that the guinea pig is entirely herbivorous The potency of the food supplement added is judged from the dail dose necessary to prevent the onset of, or to cure establishe scurvy. The antiscorbutic value of milk is dependent on the di of the animals. Lemon juice possesses a very much higher an scorbutic potency than lime juice.

H. C. R.

B. **The Necessity of Checking the Quality of Sodium Tun IND ate used in the System of Blood Analysis.** OTTO FOL soap (*J. Biol. Chem.*, 1922, **51**, 419—420).—Specimens of sodium tun dyeing, which are not alkaline to phenolphthalein contain compl that extr tes. They may be made suitable for use in the autho in a glass f blood analysis by addition of the requisite quantity the soaps

E. S.

# General and Physical Chemistry.

**The Luminescence of Incandescent Solids.** E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1922, **19**, 300—318).—Certain oxides, when heated to temperatures lying within a definite and sometimes narrow range, emit radiation in a limited region of the spectrum far in excess of the radiation emitted in that region by a black body at the same temperature. The effect is ascribed to luminescence, and is particularly marked in the case of the blue radiation from columbium oxide; the blue glow is also shown by the oxides of glucinum, magnesium, calcium, aluminium, silicon, and zirconium. Intensity–temperature curves for the red, green, and blue radiations from the oxides of samarium, gadolinium, gallium, columbium, erbium, cerium, praseodymium, and neodymium show that all except cerium emit a blue or greenish-blue glow, and all but columbium and neodymium have one or two red, green, and blue outbursts above 1000°. Luminescence is essentially different from temperature radiation, and the effect for any oxide is sensitive to slight impurities. It is considered that luminescence is probably a phenomenon of instability associated with a chemical change such as oxidation, or with the physical disturbances which the oxides undergo as they are heated.

A. A. E.

**Optics of Disperse Systems. V.** I. LIFSCHITZ and GEORG BECK (*Kolloid Z.*, 1922, **31**, 13—15; cf. A., 1920, ii, 137).—A number of misprints and errors of calculation contained in a previous paper (*loc. cit.*) are corrected. Tables of the recalculated values are given and a repetition of the measurements of the refractive index of arsenic trisulphide sol has brought the authors' measurements into agreement with those of Wintgen. The discrepancy previously found was due to a film of the arsenic sulphide separating on the prism. It is also shown that the influence of the degree of dispersion on the refraction is very small in comparison with the influence of constitution. J. F. S.

**The Mass of the Particles that Emit the Spectrum of Carbon Monoxide.** M. DUFFIEUX (*Compt. rend.*, 1922, **175**, 159—161).—On the supposition that the widening of the spectral lines emitted by a luminous gas is solely due to thermal vibration, the limit of the interference fringes which can be obtained with these lines is given by the equation $N = K\sqrt{M/T}$, where $K$ is a constant, $T$ the absolute temperature, and $M$ the mass of the luminous particles on the atomic weight scale. This method was applied to an investigation of the origin of the spectra of nitrogen and carbon monoxide. The values found for $N$ for the nitrogen lines, 3998 and 4200, were 270,000 and 274,000, respectively, whilst very concordant results averaging 313,000 were found for four of

the carbon monoxide bands, and 260,000 for the fifth band, 4123. Adopting on the one hand Lord Rayleigh's value for $K$, namely, 1·37, as an upper limit, and, alternatively, Fabry and Buisson's, 1·22, as the lower limit, $M$ for nitrogen becomes 11·6 or 14·5, and for carbon monoxide 15·3 or 18·3 for the four bands, and 10·6 or 13·2 for the fifth band. The conclusion is drawn that the two bands of nitrogen are emitted by atomic nitrogen (14), and that the four bands 5610, 5198, 4833, and 4509 are due to atomic oxygen (16), whilst the fifth band is due to carbon atoms (12), the masses of all these atoms falling well within the upper and lower limiting values obtained for $M$. G. F. M.

**The Excitation of the Enhanced Spectra of Sodium and Potassium in a Low Voltage Arc.** PAUL D. FOOTE, W. F. MEGGERS, and F. L. MOHLER (*Astrophys. J.*, 1922, **55**, 145—161; cf. this vol., ii, 4).—It is shown that the quantum theory requires that the enhanced spectra of sodium and potassium should be excited at comparatively low voltages. The experimental results demonstrate that this is the case, and clearly show the three-stage development in the spectra of these elements, namely, (1) the single pair stage, 2·1 to 5·1 volts for sodium; 1·6 to 4·3 volts for potassium; (2) the arc spectrum stage, 5·1 to 30 volts for sodium; 4·3 to 20 volts for potassium; (3) the enhanced spectrum stage, above 30 volts for sodium; above 20 volts for potassium.

A. A. E.

**The Difference between Series Spectra of Isotopes.** P. EHRENFEST (*Nature*, 1922, **109**, 745—746; cf. following abstract).—A criticism of the use of Bohr's formula for the change in frequency, $\nu$, due to the motion of the nucleus, in the case of atoms in which several electrons move round the nucleus. The formula $\nu_2 : \nu_1 = M_2/M_2+m : M_1/M_1+m$, where $M_1$, $M_2$, and $m$ are, respectively, the masses of the nuclei of the isotopes and of the electron, and $\nu_1$ and $\nu_2$ the frequencies of the corresponding lines, cannot be true in general in such cases, although it will probably be possible to derive a sufficiently approximate formula for the case of the $p$- and $d$-motions of lithium; this must be very difficult, however, for the case of the 1·5S-path. A. A. E.

**The Difference between Series Spectra of Isotopes.** N. BOHR (*Nature*, 1922, **109**, 746; cf. preceding abstract).—It is admitted that the effect of the mass of the nucleus on the spectrum of an atom containing more than one electron is a complex problem; not only may the mass effect disappear completely in such cases, but also, in the case of the motions actually met with in the emission of the series spectra, this effect may be different from that calculated for an atom with one electron. It is shown that the problem differs essentially from the problem of two bodies in celestial mechanics. The discrepancies, observed by Merton, in the wave-lengths of certain lines in the spectra of lead isotopes are considered with reference to the mass effect, and to the possibility of their being due to a slight difference in the field of force

surrounding the nucleus, arising from the difference in the internal nuclear structure of the lead isotopes. A. A. E.

**The Difference between Series Spectra of Isotopes.** J. W. NICHOLSON (*Nature*, 1922, **110**, 37; cf. preceding abstracts).—The differences found by McLennan in the spectra of the lithium isotopes are three times as great as those calculated by Bohr's formula. This large separation cannot be explained by the quantum theory, and it is suggested that the new series may be a combination series or a spark series. In an investigation on some of the simpler possible orbits in a lithium atom with only two electrons, a specially simple class of orbits was found. The principal spark-line of lithium has a value very close to λ 6708, the red line shown in the ordinary spectrum. The results appear to indicate that when there are many electrons in an atom, a ratio roughly of order 1/10 exists between the orbital radii of the two outer consecutive electrons. An immediate consequence is that the Bohr formula would never be very far wrong in its use for a rough determination of the separation to be looked for in the spectra of isotopes.
A. A. E.

**The Vacuum-spark Spectra of the Metals.** EDNA CARTER (*Astrophys. J.*, 1922, **55**, 162—164).—Vacuum-spark spectra of calcium, magnesium, cadmium, titanium, and iron were obtained, the iron spectrum being also photographed on a dyed film from λ 4000 to λ 6600 Å.; the new spectra show no striking new characteristics. The vacuum-spark spectrum of calcium and magnesium is practically identical with the spark spectrum in air; with cadmium, and particularly with titanium, the arc lines are more intense. In the case of iron, the vacuum-spark spectrum is more like the arc spectrum than the spark spectrum. In general, the vacuum-spark spectra resemble the luminescence spectra produced by cathode-ray bombardment in a high vacuum; the conditions of emission in the two cases are considered to be very similar. A. A. E.

**The Limits of Absorption *L* of the Elements Barium to Antimony.** LINDSAY (*Compt. rend.*, 1922, **175**, 150—151).—The limits of absorption, *L*, of the elements barium, cæsium, iodine, tellurium, and antimony were measured by means of a vacuum spectrograph, using a prism of calcite, and a 0·1 mm. slit. The current used was between 10 and 50 milliamperes, at such a voltage that the second order did not appear in the spectral region studied, for example, 8000 volts for antimony. The screens consisted of a thin sheet of paper which had been dipped in a saturated solution of a suitable compound of the element. The following results, expressed in units of $10^{-11}$ cm., were obtained.

| | $L_1$. | $L_2$. | $L_3$. |
|---|---|---|---|
| Barium | 2357·7 | 2199·5 | 2060·2 |
| Cæsium | 2467·8 | 2307·3 | 2160·5 |
| Iodine | 2712·4 | 2548·3 | 2381·9 |
| Tellurium | 2847·0 | 2683·7 | 2502·6 |
| Antimony | 2994·5 | 2831·0 | 2632·7 |

A comparison of the values of the Sommerfeld doublet (expressed as $1/\lambda$) for the limits of absorption ($L_2-L_1$) and the two lines $\beta_1-\alpha_2$ measured by Hjalmar shows a very satisfactory agreement.

G. F. M.

**The Variations of the Spectrum of the Mercury Arc with the Conditions of Emission.** St. Procopiŭ (*Compt. rend.*, 1922, **175**, 217—219).—If the arc is produced in a vacuum with a current of 14—15 volts and 1·9 amperes, the spectrum contains more lines towards the extremity of the ultra-violet than if a more powerful current (65 volts, 3·5 amperes) is used with a correspondingly increased vapour density. Under both conditions of current, the cathodic spectrum is richer in lines than the anodic, and with the higher voltage the cathodic lines become diffuse, sometimes so much so as to form a continuous spectrum. If the arc is struck in air, under water, or especially in coal gas, the lines of the two secondary series are weakened and widened compared with the lines of the vacuum arc, this being the more pronounced the higher the position of the line in the series. The line 2537 appears strongly inverted in the three media, and a number of lines are strengthened, notably 3984, 2857, 2848, and 2224. The author considers that the widening of the lines is related to the Stark effect and explainable by the assumption of an intermolecular electric field, whilst the weakening or disappearance of certain lines when the arc is struck in air, water, etc., may be explained by Bohr's theory.

G. F. M.

**Fine Structure of Röntgen Spectra.** Adolf Smekal (*Sitzungsber. Akad. Wiss. Wien*, 1921, **130**, 25—30; from *Chem. Zentr.*, 1922, i, 240; cf. A., 1921, ii, 292, 615).—The scheme for the *L* series can only be tested for tungsten since in this case alone are sufficient experimental data available. There are five *M* layers and at least five *N* layers. G. W. R.

**The Absorption Spectrum of Potassium Permanganate.** A. Hagenbach and R. Percy (*Helv. Chim. Acta*, 1922, **5**, 454—468).—Spectrophotometric measurements were made of the absorption of aqueous potassium permanganate solutions at twelve dilutions from $2^{-6}$ to $2^{-17}$ mol. per litre at sixty-one points in the visible spectrum between wave-lengths 438 and 701 $\mu\mu$. From the results, curves were plotted in which the percentage absorption was plotted against the wave-length at each dilution, and from the curves obtained the positions of the absorption bands were deduced. New figures are given for the wave-lengths of the eight known bands, differing slightly in some instances from those given by Formánek. The new figures are 4388, 4537, 4695, 4866, 5050, 5249, 5461, 5695. These bands are related in such a manner that there is a constant difference between the oscillation frequencies of successive members of the group. This law has not previously been observed to hold for an inorganic substance. The broad band which Formánek ascribed to the wave-length 6370 has been resolved into four bands at 5949, 6264, 6528, 6862. These then

form a continuous series with the other eight bands. The Beer-Lambert law was found to hold within the limits of 5%. E. H. R.

**Structure of the Second Cyanogen Band.** JUNZÔ ÔKUBO (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 55—86).—The second cyanogen band radiated by the ordinary carbon arc in air was examined under higher dispersion and resolving power than that used by previous investigators. The wave-length of all lines lying between the first head at λ 4216 Å. and λ 3900 Å. (about 1555 in all) were measured and calculated in international units. This band contains many doublet lines with close components, some of which have been previously described as singlets. Three remarkable series were traced, one triplet series beginning from the first head and two closed doublet series beginning from the second head. The intensity distribution in these series is described. The wave-length of the heads of cyanogen bands were measured and some simple relations are shown to exist between the differences in the ratios of the wave numbers of the heads; for example, the differences in the ratios for successive heads are generally in an arithmetical progression. T. H. B.

**Absorption Spectra of Triphenylmethane Colouring Matters.** EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 461—464).—The author has shown (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], **27**) that triphenylmethane colouring matters, when dissolved in water, alcohol, ether, benzene, glycerol, toluene, or xylene, exhibit absorption curves of similar types with maxima which undergo gradual displacement as the molecular weight of the solvent increases. Solutions of 19 of these colouring matters in water and in methyl, ethyl, *iso*butyl, and amyl alcohols have now been examined spectroscopically by the diffusion method (A., 1920, ii, 720), the positions of the mid-points of the two absorption bands being tabulated. With the alcoholic solutions the velocity of diffusion is greater than with those in other solvents, this velocity diminishing as the molecular weight of the alcohol increases. The diffusion of some of the compounds examined is characterised by two distinct phases: the first consists in a rapid propagation of the coloration with a very low gradient of the concentration, the spectrum showing only one of the characteristic bands which assumes constant breadth; the original surface of separation remains and gives rise to a second, slower diffusion, as a result of which the absorption curve characteristic of this group of compounds becomes complete. That this phenomenon of double diffusion appears to be due to two different atomic groupings is supported by other evidence to be published later.

The gradual displacement of the maxima of the absorption curves as the molecular mass of the alcoholic solvent increases is observed with all the compounds examined with the exception of uranine and rhodamine-B. T. H. P.

**The Calculation of the Colour of the Azo-dyes and Related Coloured Substances.** JAMES MOIR (T., 1922, **121**, 1555—1562).

**Absorption Spectra of Benzeneazophenol and its Derivatives.** Alpheus W. Smith and C. E. Boord (*J. Amer. Chem. Soc.*, 1922, **44**, 1449—1455).—The absorption spectra of benzeneazophenol and each of the three isomeric tolueneazophenols, chlorobenzeneazophenols, and nitrobenzeneazophenols have been measured in alcohol and in alcohol containing sodium hydroxide. The measurements were made by the visual metbod and in all cases continuous absorption curves were obtained. It is shown tbat the suhstitution products absorb light more strongly in the visible region than does benzeneazophenol, and the alkali salts more strongly than the free dyes. The order of absorption for the isomerides in the dilutions examined is para > meta > ortho, except in the case of the nitro-derivatives, when it becomes para > ortho > meta. The deviation of the latter derivatives may be due to a difference in structure. The changes in absorption brought about by substitution are discussed briefly in the light of McCleland's mutual induction theory of absorption of light. J. F. S.

**Disturbance of the Power of Fluorescing of Fluorescent Solutions by Light, and the Photochemical Equivalent Law.** Peter Pringsheim (*Z. Physik*, 1922, **10**, 176—184).—The change in the intensity of the fluorescence of fluorescein, eosin, and other substances in aqueous, alcohol, glycerol, and amyl alcohol solutions, when submitted to an intense beam of ligbt, has been investigated. It is shown that the disturbance of the power of fluorescence, discovered by Perrin (A., 1918, ii, 418; 1919, ii, 177) and investigated by Wood (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 362; this vol., ii, 334) is due to the concentration of the acting light, a result also obtained by Wood. Of two solutions of equal concentration, that with the weaker fluorescenee is changed more rapidly than the other, and of two solutions with the same intensity of fluorescence and with identical absorption and fluorescence spectra, the one may be changed more rapidly than the other and thereby a different product produced. The fluorescence spectrum of a newly-formed substance is displaced in the same sense as the absorption spectrum of this substance. The intensity of fluorescence is not markedly changed at low temperatures, but the chemical reaction is practically inhibited. For these reasons, the hypothesis of Perrin (*loc. cit.*), according to which fluorescence is an attendant phenomenon of chemical change, cannot be maintained. On the other hand, there is the second possibility, that either fluorescence or chemical change is of importance for the validity of the photochemical equivalent law. J. F. S.

**The Influence of Constitution on the Rotatory Power of Optically Active Substances. XV. A New Constant for Calculating the Curve of Rotation-dispersion.** H. Rupe (*Annalen*, 1922, **428**, 188—198).—In place of the customary magni-des $\lambda\alpha$ and $\lambda_0^2$, it is now proposed to use $\lambda\alpha$ and $\lambda_0$, and, in par-ar, their product, $\lambda\alpha \cdot \lambda_0 = k$, which is termed the "Rotation-sion Product," and is signified by the letters "*P.R.D.*" It (by reference to camphor derivatives) that the *P.R.D*'s

exhibit a fair degree of constancy for a series of substances of the same "optical type." C. K. I.

**Molecular Æolotropy in Liquids.** C. V. Raman (*Nature*, 1922, **110**, 11).—In experiments with many liquids on the molecular scattering of light, the scattered beam in a direction transverse to the primary rays shows a large admixture with unpolarised light. It is therefore suggested that the polarised and unpolarised parts of molecularly scattered light may arise in two distinct ways, the former being a mass effect, and the latter a molecular effect. Passing from the condition of vapour to that of liquid considerably increases the ratio of unpolarised to polarised light, as has been experimentally shown in the cases of ethyl ether, benzene, and chloroform; such increase would naturally be in proportion to the number of molecules per unit volume. Moreover, when a substance is in the state of vapour under small pressures, both the positions and orientations of its molecules are absolutely at random, and assuming the molecules to be æolotropic, the degree of imperfection of polarisation of the light scattered by it may be calculated; in the liquid state, however, the packing of the molecules is so close that their ordering in space is no longer at random, but the orientations may still be considered to be arbitrary. Viewed in this way, the same results are obtained. A. A. E.

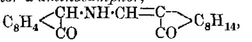
**The Rotatory Power of Crystals and Molecular Rotatory Power.** Louis Longchambon (*Compt. rend.*, 1922, **175**, 174—177).—A comparison of the crystalline rotatory power with the molecular rotatory power expressed as $[\alpha]d/100$, where $[\alpha]$ is the specific molecular rotation, and $d$ the density of the crystal, showed with the substances examined, including camphor, sucrose, rubidium, and ammonium tartrates, and ammonium molybdomalate, no definite constant relationship. On the other hand, the rotatory dispersions, that is to say, the ratio of the rotations for two given spectral lines, exhibited practically constant values, in spite of great variations in the rotatory power in passing from the liquid to the crystalline state. In the case of camphor, remarkably constant values were obtained for the rotatory dispersion in solution in ethyl ether, and in hexane, and in the liquid, gaseous, and crystalline states. If it is admitted with Traube and Landolt that there is a structural rotatory power in crystals superimposed on a molecular rotatory power, the former must therefore present the same rotatory dispersion as the latter, which, a priori, does not seem reasonable. The only alternative to this is that there is no structural rotatory power, and the rotatory power of the crystal is therefore the molecular rotatory power in a determined direction, it being established that the rotation is variable with the direction of observation. The rotatory dispersion, however, is in all cases independent of the direction of observation. G. F. M.

**A Case of Total Anomalous Rotation-Dispersion.** H. Rupe and H. Schmid (*Helv. Chim. Acta*, 1922, **5**, 437—443).—Tschugaev and Glinin (A., 1912, ii, 1020) consider that the cause of anomalous

rotation-dispersion is to be found in the influence of the optical superposition of several asymmetric carbon atoms on an absorption band in the ultra-violet. The authors dispute this hypothesis, and suggest that the phenomenon is due to the disturbing influence of unsaturated residues on the asymmetric carbon atom. In agreement with this view, they find that triphenylmethyl-α-aminocamphor exhibits total anomalous rotation-dispersion in benzene and in acetone solution, whilst the condensation product of α-aminocamphor with hydroxymethylenecamphor is normal.

*α-Triphenylmethylaminocamphor* is prepared by condensing triphenylchloromethane with α-aminocamphor, m. p. 153—154°, $[\alpha]_C$ −1·34°, $[\alpha]_D$ −1·68°, $[\alpha]_{Hg}$ −1·68 (λ=546·3), $[\alpha]_F$ −2·13° in benzene.

*Methylenecamphor-α-aminocamphor*,



forms white to pale yellow leaflets, m. p. 228—230° (decomp.); $[\alpha]_C$ +90·51°, $[\alpha]_D$ +121·8°, $[\alpha]_{Hg}$ +151·7°, $[\alpha]_F$ +211·4° in benzene.

E. H. R.

**Coagulation of Colloids by Sunlight.** P. B. Ganguly and N. R. Dhar (*Kolloid Z.*, 1922, **31**, 16—19).—The action of sunlight on colloidal gold, silver, platinum, copper, sulphur, selenium, a number of colloidal sulphides, hydroxides, and complex colloidal solutions, both pure and in the presence of protecting colloids, has been investigated. In most cases, it is shown that sunlight increases the rate of coagulation. In the case of the metallic sulphides, the sensitiveness toward sunlight follows the order: arsenic, cadmium, mercury, and antimony sulphide, whilst in the presence of gelatin as protecting colloid the order is: nickel, platinum, zinc, gold, iron, cobalt, and silver sulphide. In the case of a manganese dioxide sol containing 0·3 gram of manganese dioxide per litre, sunlight has the same coagulating action as 2·5 c.c. of a 2*N*-solution of copper sulphate acting on 25 c.c. of the sol. Colloidal solutions of stannous, bismuth, lead, manganese, and ferrous sulphides, when acted on by sunlight in the presence of air, are oxidised with the formation of colloidal sulphur, which on further action of light is coagulated.

J. F. S.

**Decomposition of Iodoform in Solutions by Means of Radiant Energy.** E. H. Butler (*Chem. News*, 1922, **125**, 38—39).—Iodoform in benzene or carbon tetrachloride solutions is decomposed by light, but in alcoholic solution there is no decomposition.

J. F. S.

**Thermotropy.** José Rodríguez Mourelo (*Anal. Fís. Quím.*, 1922, **20**, 139—145).—Some experiments are recorded on the effect of heat on the phototropy of certain sulphides. Phototropy is diminished by low temperatures and increases with rise of temperature up to a maximum, after which it diminishes. Phototropy may, under certain conditions, be induced by simple heating in the absence of light.

G. W. R.

**Conductivity of the Latent Image.** A. G. RABINOVICH *J. Physical Chem.*, 1922, **26**, 577—590).—With the object of urnishing evidence as to the nature of the nndeveloped photo-raphic image, the author has determined the electrical resistance f celluloid photographic films aud silver bromide gelatin emulsions oth before and after illumination. The results show that the esistance undergoes no change measurable by the most sensitive ıethods, and consequently this method throws no light on the ature of the latent image. The electrical conductivity of a dry lm 5×10 mm. at 18—20° is of the order $10^{-11}$/ohm cm. and the emperature coefficient about 10% per degree, whilst the specific onductivity of a silver bromide gelatin emulsion at 22° is 8·0× $0^{-4}$ohm$^{-1}$ and the temperature coefficient 3% per degree.

J. F. S.

**Absorption and Dispersion of Radiation.** FRITZ WEIGERT *Z. physikal. Chem.*, 1922, **44**, 414—444).—A theoretical paper in hich the absorption and dispersion of radiation are considered in he light of modern work. The experimental results of the effects f linearly polarised light on the different photo-sensitive systems nd the adaptation of the system to the colour of the exciting adiation are mainly considered. It is shown that for these effects ot a single molecule, but always a whole system of numerous nordered and closely-packed molecules of different types, is esponsible. The actual process of adsorption, which is closely onnected with the adaptation, can ouly occur through the simul-ıneous action of different molecules or molecular groupings. The ombination of the individual parts of such a closely packed aggre-ate occurs through electrons in an internal photo-electric effect, in hich an electron from a molecule is projected in the direction of ıe radiation with an energy given by the relationship $1/2mv^2=h\nu$, ıd taken up by an electron receiver. The frequency and direction the absorbed radiation is determined by the distance between ıe two molecules and their relative orientation; since almost l combinations are possible, the adaptation to the colour and irection of the radiation is practically unlimited. The absorption ectrum varies with the spatial arrangement and the relative roportion of the electron emitter and receiver, in the sense that the ands are displaced toward the red when the proportion of receivers greater than that of emitters, and toward the blue when the roportion is the reverse. It is possible by spectrometric measure-ıents to differentiate the two constituents. The inconstancy of ıe absorption of the chief coloured substances, the finely divided isperse systems, organic dyes, and inorganic complex compounds ın be shown in the case of the photo-chlorides, cyanin collodion yers, and the blue copper–ammonia complexes respectively. In l these cases, Beer's law does not hold, and the reason for this is be found in the method of action of the electron emitters and ceivers, so that here a perfectly general phenomenon is to be und. The emitters expel their electrons with an energy $h\nu$ hen they encounter a radiation of frequency $\nu$ in a perfectly

definite phase, which probably is the maximum of the magnetic displacement. The electron then probably takes a cometary path, and if, at the limit of its path, it meets an electron receiver it stays there, and the system now richer by one energy quantum takes from the radiation the amount of energy still failing. In the more likely case where the electron does not meet with a receiver, it returns to the emitting molecule and thereby emits an impulse wave of the frequency $\nu$. This impulse is, however, emitted with a certain delay, which is equal to the time of flight of the electron. During the passage of radiation through a material system, a diminution of the light velocity is recorded which is greater the greater the frequency, for the electron has a longer path and the time of flight is longer. Here is to be found a meaning for normal dispersion. When the time of flight is exactly a half period of the radiation, the emitted impulse destroys the exciting radiation entirely by interference. If this corresponds with the characteristic frequency of the substance, then the radiation does not pass through the medium, and a zero velocity of light and an infinitely large index of refraction are observed. When the time of flight is only a little larger than the half period, then it appears as though the emitted wave commences before the exciting radiation disappears. Here there is an apparent increase in the velocity of light and abnormal dispersion. This repeats itself when the time of flight $t_\nu$ is equal to an odd multiple of the half period which is expressed by the formula $t_\nu=(n-1/2)1/\nu$. The abnormal dispersion of spectrum lines is probably explained by this formula, when for $n$ the natural series of numbers is inserted. J. F. S.

**Determination of the Velocity of the α-Rays of Polonium.** (MLLE) IRÈNE CURIE (*Compt. rend.*, 1922, **175**, 220—222).—The velocity of emission of the α-rays of polonium was determined by the magnetic deviation method, the distance between the impressions produced by the α-rays on a photographic plate in the presence and in the absence of the magnetic field being measured with great precision by means of the instrument used for spectrographic measurements, from which it was calculated that the velocity of the rays is $1593\times10^9$ cm. per second, and the ratio of the emission velocities of the α-rays of polonium compared with those of radium-*C* is accordingly 0·829. This is in close agreement with the value 0·826 given for the ratio of the cube roots of the penetrating power of the α-rays of these two elements.

G. F. M.

**α-Particles as Detonators.** G. H. HENDERSON (*Nature*, 1922, **109**, 749).—If it is considered that when an α-particle passes through matter, the matter in its proximity is momentarily raised to a high temperature, the detonation of certain unstable substances would be expected to take place on exposure to the action of these particles. Air-dried nitrogen iodide is detonated in this way. pera detonation is not caused by the first α-particle which happens tropyike the substance, but appears to be a probability effect.
in the A. A. E.

**Multiple Valency in the Ionisation by α-Rays.** T. R. WILKINS (*Physical Rev.*, 1922, **19**, 210—220; cf. Millikan, Gottschalk, and Kelly, *ibid.*, 1920, **15**, 157; *Proc. Nat. Acad. Sci.*, 1919, **5**, 591).—Slight modifications were introduced into Millikan's oil-drop method for determination of the valency of individual ions, polonium being used instead of radium bromide as a source of α-rays. In air, not more than 3% of the positive ions could have been doubly charged; the number was probably considerably smaller. In helium, a determination was made of the variation of the number of "doubles" with the range; the maximum proportion was found to be about 10% for the range of maximum ionising power. The corresponding figure for hydrogen was 0·5%. The relative stopping power for α-rays of air and helium was found to be about 3·8, a result which is in agreement with the Bragg–Kleeman law. A. A. E.

**Theory of Röntgen Spectra. II.** ADOLF SMEKAL (*Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 635—660; from *Chem. Zentr.*, 1922, i, 240).—The error introduced by the use of the Loschmidt number in the standard value for the lattice constant of sodium chloride is considered. Attention is also directed to a theoretical $L_{\alpha}$ arrangement which takes account of the relativity correction. The hypothesis used in the proof of the electron ring theory may be reduced to Bohr's frequency hypothesis. The presence of three electrons in the *K* ring follows qualitatively from the assumption of a spacial arrangement of electrons in the sheath. The determination of the quantum conditions of the *L* and *M* electrons permits the number of *L* and *M* absorption edges to be obtained. G. W. R.

**Röntgen Spectra and Chemical Valency.** GREGOR WENTZEL (*Naturwissenschaften*, 1922, **10**, 464—468).—A discussion of the dependence of the *K* absorption limits of chlorine and phosphorus on the valency as observed by Lindh (*Compt. rend.*, 1921, **172**, 1175) and Bergengren (A., 1920, ii, 654). It is probable that the properties of the *K* limits of titanium, vanadium, and chromium reported by Fricke (A., 1921, ii, 6) are due in so far as this structure extends to the weaker part to the presence of ions of different valency. The structure of the *K*-β line of the light elements is explained similarly (cf. Hjalmar, A., 1920, ii, 655; 1921, ii, 145, 292). CHEMICAL ABSTRACTS.

**Radium Synthesis of Carbon Compounds from Air.** F. HARRISON GLEW (*Nature*, 1922, **109**, 714).—Quartz or glass fibres, supported immediately above an uncovered radioactive surface, the whole being enclosed in a box in a dark room, become covered in a few days with a white, viscid liquid, tending to form droplets. Prolonged exposure causes increase in size of the droplets, coloration to dark brown, and a tendency to solidify with irregular contraction. The gaseous emanation of radium seems to be necessary, since deposits cannot be obtained by using α-, β-, or γ-rays, either separately or in combination. A chemical examination of the products has not yet been made. A. A. E.

**An Attempt to Influence the Rate of Radioactive Disintegration by Use of Penetrating Radiation.** G. HEVESY (*Nature*, 1922, **110**, 216; cf. Ellis, this vol., ii, 339).—It is assumed that the emission of $\gamma$-rays from the nucleus of the atom precedes the disintegration process. If, therefore, the nucleus could be induced to take up a $\gamma$-ray impulse supplied by an exterior source, it would mean a change in its stability, and so most probably a change in the rate of its disintegration. Experiments with uranium in radioactive equilibrium with uranium-$X$, and with radium-$D$ in equilibrium with radium-$E$, failed to show a change in $\beta$-radiation greater than 0·1% and 0·2%, respectively. A. A. E.

**Measurement of the Resonance, Radiation, and Ionisation Potentials of Several Gases and Vapours.** PAUL EDWARD BOUCHER (*Physical Rev.*, 1922, **19**, 189—209; cf. Mohler and Foote, A., 1920, ii, 464).—A modification of Compton's variable-area electrode was employed. The resonance potentials were obtained from the difference in voltage between successive peaks of the resonance curves; the ionisation potentials from the Lenard current–voltage curves corrected as to zero by the resonance curves; the relative importance of radiation and ionisation at various voltages from the ratio of the Lenard currents obtained with the plate to the corresponding currents obtained with the gauze electrode having only one-fourth the area. The critical resonance potentials, potentials at which radiation is predominant, and ionisation potentials, in volts, accurate to about ±0·1 volt except in the case of toluene, are as follows: hydrogen, 10·1, 10·1—13·6, 13·6, and 15·6; nitrogen, 8·4, 8·4—15·8, 15·8; oxygen, 8·0, none, 14·0; ethyl ether, 6·6, 8·1—10·1, 13·6; benzene, 6·0, none, 9·6; toluene, 6·2±0·2, none, 8·5±0·5; xylene, 6·5, none, 10·0; chloroform, 6·5, none, 11·5. A. A. E.

**The Effect of Oxygen and Hydrogen on the Emission of Electrons from Hot Platinum.** LAURICE L. LOCKROW (*Physical Rev.*, 1922, **19**, 97—113).—By using a tube with a platinum cylinder surrounding a V-shaped filament, it was found that the effect of oxygen and air was slightly to decrease the emission, the observations of Richardson, Wilson, and others being thereby confirmed. The effect is, however, temporary and is not due to the formation of heavy ions, neither is there evidence of the formation of an oxide of platinum. Pure hydrogen probably has no effect on the emission from pure platinum, the observed effects, although considerable, being ascribed to impurities. Richardson's constants for pure platinum were found to be: $A=9900$; $b=52000$, whence the thermionic work function for platinum is 4·46 volts. These values are lower than those obtained by other methods, and are subject to errors inherent in the resistance method of measuring temperatures. A. A. E.

**Behaviour of Free Electrons toward Gas Molecules.** H. B. WAHLIN (*Physical Rev.*, 1922, **19**, 173—186).—To account for the appearance of abnormal negative mobilities at low pressures,

Wellisch (*Amer. J. Sci.*, 1915, [iv], **39**, 583; 1917, [iv], **44**, 1; A., 1917, ii, 352) assumes that in order to form an ion an electron must have more than a certain amount of energy, whilst Thomson (*Phil. Mag.*, 1915, [vi], **30**, 321) considers that it must have made, on the average, *n* impacts. The author finds that when the energy of the electrons is increased the number of ions is not increased; hence Thomson's theory is preferred. The Thomson constant *n* was determined for carbon monoxide, ammonia, ethylene, acetylene, ethane, ethyl chloride, and chlorine. The results, which depend on the values assumed for the mobility of the electron in the various gases, indicate a progressive decrease in the value of *n* in the above order from about $10^6$ for carbon monoxide to $10^3$ or less for chlorine. It is concluded that electronegative gases attach electrons more readily than do electropositive gases, and that the degree of saturation of hydrocarbons has but little effect. The mobility of negative ions in chlorine, ethane, and ethylene was found by Rutherford's method to be, respectively, 0·73, 1·30, and 0·91 cm./sec./volt/cm. at atmospheric pressure. A. A. E.

**Piezo-electricity of Potassium Sodium Tartrate Crystals.** E. KILBURN SCOTT (*Trans. Faraday Soc.*, 1922, **17**, 748—752).—An account of the piezo-electric properties of Rochelle salt crystals, based on the recent work of A. McLean Nicolson. Suitable crystals are best prepared by the hurried cooling of a saturated solution of potassium sodium tartrate, in which a temperature gradient is established and seed crystals are immersed. Piezo-electric properties are best developed in crystals having one side slightly concave and the other convex, and in which the "hour-glass" marking is developed. An average-sized crystal weighs 100 grams. The piezo-electric effect is very pronounced when the crystal is dried in 90% alcohol for twenty-four hours, then in 100% alcohol for about four hours, and afterwards baked at 40° for several days. In the case of crystals showing the "hour-glass" structure, the piezo-electric effect is best developed by the application of a twisting couple about the principal axis of the crystal. Potentials as high as 500 volts can be developed, and the crystals are readily applicable to the reproduction and transmission of sounds.

J. S. G. T.

**The Electrodeless Discharge in certain Vapours.** J. K. ROBERTSON (*Physical Rev.*, 1922, **19**, 470—477; *cf.* A., 1921, ii, 668).—The effect of the discharge, which was produced by electromagnetic induction, varied with the vapour pressure and with the *E.M.F.* Potassium at 250—300° gave a bright ring with a spectrum including seven or more members of each subordinate series. Sodium above 300° gave a bright yellow discharge showing the *D*-lines, four members of the diffuse series, and three members of the sharp series. Lithium up to 500° gave only a feeble discharge due to impurities. Kowalski's observations in the case of mercury were confirmed and extended. A white ring discharge (at 70—110°), at first dazzling, became fainter and was followed (at 110—115°) by a green glow of which the spectrum showed

a few lines superimposed on a continuous band extending from the violet to the yellow. The glow may be associated with polyatomic molecules formed at the higher vapour pressures. Iodine at $-5°$ to $+5°$ gave a pale yellow ring showing a band spectrum, changing with increase in the spark gap to a green, pink-bordered ring with a line spectrum. The change may be due to dissociation of molecules into atoms. It is suggested that the method may be applied to the investigation of isotopy. A. A. E.

**Construction of Platinum Film Electrodes and their Method of Use.** A. EILERT (*Z. angew. Chem.*, 1922, **35**, 445—446).—The method of preparing durable electrodes from burnt-in layers of platinum is described. A thin piece of platinum wire is sealed into the end of a glass tube and while the glass is still soft pushed inward, so that a deep depression is produced. This is allowed to cool and then coated with one of the numerous platinising liquids in such a way that both the outside walls of the tube and the walls of the depression are thickly coated. The tube is then heated, at first cautiously and then to the softening point. In this way, a layer of platinum is burnt into the glass and is in good contact with the platinum wire. A drop of mercury inside the tube makes contact with the rest of the apparatus. Measurements are given to show the durability and permanence of such electrodes. J. F. S.

**Construction of Platinum Film Electrodes and their Method of Use.** A. EILERT (*Z. angew. Chem.*, 1922, **35**, 452—455).—Examples are given of the application of the film electrodes described in the preceding abstract. Only in the case of film electrodes used in the electro-analysis of metals do the films require periodical renewal. A simplified method of electrometric titration of solutions of salts of weak acids is described. J. S. G. T.

**Sodium Amalgam Electrode for the Determination of Sodium Ion [Concentration].** BENJAMIN S. NEUHAUSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1411—1416).—The trustworthiness of a sodium amalgam electrode for the measurement of the concentration of sodium ions has been investigated by measuring cells of the type NaHg|NaCl($c$)||sat. KCl||sat. KCl,$Hg_2Cl_2$|Hg at 25°. Further measurements have also been made with sodium chloride containing various amounts of potassium, ammonium, calcium, and zinc chlorides. The electrode was made up in a vessel similar to that employed by Lewis and Kraus (A., 1910, ii, 1027), except that at the bottom of the vessel there was a tap for draining off the amalgam which had dropped from the electrode. An amalgam containing about 0·16% of sodium was used and measurements were made against the normal electrode. The following values were obtained for the concentrations of sodium chloride stated: 0·20$N$, 2·1483 volt; 0·10$N$, 2·1650 (2·1649); 0·02$N$, 2·2035 (2·2042); 0·01$N$, 2·2198 (2·2213); the values in brackets are the *E.M.F.* values calculated from the value obtained for the 0·20$N$-solution. Further readings were made in each case at five-minute intervals to see how rapidly

the electrode lost its sodium, and then a new surface was produced and a further reading made. The following figures show the type of change: 0·2*N*-*sodium chloride*, voltage at start, 2·1482; after five minute intervals, 2·1482, 2·1480, 2·1476, 2·1470, 2·1460; new surface, 2·1483. Long series of measurements are recorded for solutions containing the salts mentioned above, gelatin, serum, and proteins and no difficulties were observed in the work.

J. F. S.

**Modification of the Clark Hydrogen Electrode Vessel to permit Accurate Temperature Control.** GLENN E. CULLEN (*J. Biol. Chem.*, 1922, **52**, 521—524).—The Clark electrode vessel (A., 1916, ii, 75) is provided with an additional opening by means of which a thermometer may be inserted in the solution. E. S.

**Electrolysis of Aqueous Solutions of Alkali Nitrites with a Lead Anode, and an Electrometric Determination of the Constitution of the Complex Ion formed.** F. H. JEFFERY (*Trans. Faraday Soc.*, 1922, **17**, 709—718).—In continuation of previous work on the electrolysis of aqueous sodium nitrite solutions employing a silver or copper anode (A., 1920, ii, 662; 1921, ii, 374), the author has investigated the phenomena occurring when a pure lead anode is employed in such electrolysis. A cathode of smooth platinum was used. The strength of the anolyte solution varied from 6·9 grams to 27·6 grams of sodium nitrite per 100 grams of water. The temperature was maintained at 17—18°, and the anode area was 100 sq. cm. The current ranged from 0·099 to 0·77 ampere. Lead was in no case deposited on the cathode, but was dissolved at the anode, forming a complex ion which gave a bright orange colour to the anolyte. For small concentrations of lead in alkali nitrite solutions, probably the only plumbo-nitrite complex formed is $[Pb(NO_2)_4]''$. Crystals of $Pb(NO_2)_2,H_2O$ are in equilibrium with solutions obtained from anolytes of certain concentrations. Solid solutions derived from aqueous solutions containing potassium-, nitrate-, and nitrite-ions and the plumbo-nitrite complex are orange-coloured, but more red than the orange of lead nitrite. It is suggested that the complex exists as a definite atomic group in such crystals. J. S. G. T.

**Electrolysis of Sodium Silicate Solutions.** JAMES FREDERICK SPENCER and KATHLEEN PROUD (*Kolloid Z.*, 1922, **31**, 36—37).—Orthosilicic acid may be prepared by the electrolysis of a 50% solution of sodium silicate in a divided cell, using a heavy anode current density. The cathode employed was a platinum dish 7·5 cm. in diameter, and this contained a small porous pot which held the anode, a coil of platinum wire of 1·80 cm.$^2$ surface. A current of 9 amperes was used, and this fell rapidly until no current passed, due to the formation of an insulating layer of orthosilicic acid on the anode. On bending the wire, the deposit fell away and the current again passed. The product is glass-like in appearance, entirely insoluble in water, and stable in the air.

J. F. S.

**The Electrochemistry of Non-aqueous Solutions. I. Measurement of Current-density and Potential Difference in the Electrolysis of Metallic Salts in Pyridine.** ROBERT MÜLLER (*Monatsh.*, 1922, **43**, 67—74).—A form of electrolytic cell suitable for these measurements is described, and the preparation of an appropriate standard electrode investigated. The element $Ag/0{\cdot}1N\text{-}AgNO_3$ in pyridine has a potential (measured with reference to the calomel electrode) of $+0{\cdot}28$ volt (H=0), and the element $Ag/0{\cdot}1N\text{-}AgNO_3$ in pyridine/$NH_4NO_3$ saturated solution in pyridine, has $+0{\cdot}26$ volt (H=0). C. K. I.

**The Electrochemistry of Non-aqueous Solutions. II. Decomposition Potential and Electrode Potentials in the Electrolysis of Pyridine Solutions of Silver Nitrate, and the Potential of Silver in these Solutions.** ROBERT MÜLLER and ALOIS DUSCHEK (*Monatsh.*, 1922, **43**, 75—80; cf. preceding abstract).—The decomposition potentials are: $0{\cdot}1N\text{-}AgNO_3$, 2·15 volts; $N\text{-}AgNO_3$, 2·05 volts; saturated-$AgNO_3$, 1·95 volts. The silver potentials (invariant with current density) are: $Ag/0{\cdot}1N\text{-}AgNO_3$, $+0{\cdot}24$ volt; $Ag/N\text{-}AgNO_3$, $+0{\cdot}33$ volt; Ag/saturated $AgNO_3$, $+0{\cdot}33$ volt referred to the hydrogen electrode. The anodic potential differences are functions of the current density for each of the above concentrations. C. K. I.

**Variations in the Magnetic Susceptibility of Oxychromic Salts with Addition of Sulphuric Acid.** B. CABRERA and S. PIÑA DE RUBIES (*Anal. Fis. Quím.*, 1922, **20**, 175—181).—The effect of the addition of sulphuric acid to solutions of an oxychromic salt is twofold and results in a depression followed by an elevation of the magnetic constant. In the experiments recorded the variations of the magnetic constant of solutions of an oxychromic salt with time were followed for different values of the ratio $H^{\cdot}/Cr^{\cdot\cdot\cdot}$. For high values of this ratio, the change is so rapid that only the elevation in the magnetic constant is noticeable. For low values of the ratio, the initial depression is clearly shown by the experimental curves. G. W. R.

**A New Adjustable Thermostat for all Temperatures between 0° and 100°.** SAMUEL JUDD LEWIS and FLORENCE MARY WOOD (*Trans. Faraday Soc.*, 1922, **17**, 696—700).—A form of thermostat employing a toluene–mercury thermo-regulator of the type dne to Barnes and to Gouy is described. The individual parts of the apparatus were independently mounted on a framework extending the length of the thermostat. The surface of the mercury used in the electrical relay employed was covered with glycerol. The dimensions of the thermostat were $24'' \times 16'' \times 14''$, and any desired temperature was attained from cold in an hour and a half. After a further half hour, the temperature did not vary by more than 0·01°. J. S. G. T.

**Electric Heating and Controlling Apparatus for a small Thermostat.** S. O. RAWLING (*J. Soc. Chem. Ind.*, 1922, **41**, 250—251T).—An electric heating and controlling apparatus is

described by means of which the steady temperature of a small thermostat may be speedily fixed at any point between 25° and 40° without making troublesome readjustments of the apparatus. The current is supplied through two resistances, $R_1$ and $R_2$, in series to the heating resistance, and a toluene or calcium chloride regulator is so arranged that the second resistance may be cut out or left in the circuit as the temperature demands. The resistance $R_1$ is of such a size that when the current passes through it and the heater alone too much heat is developed, but when the current passes through $R_1$, $R_2$, and the heater, insufficient heat is supplied to keep the temperature at the required point. The thermo-regulator consists of a long bulb from the neck of which a side arm slopes downward and connects with the middle of a U-tube. The U-tube itself is divided into two parts by means of a glass seal through which a platinum wire is fused. One arm of the U-tube is provided with a short length of capillary tubing of about 1 mm. bore. A side tube is fitted above the top of the capillary and a rubber stopper fitted into the widened end of the U-tube carries a platinum electrode, which projects about 1·5 cm. into the capillary tube. The upper end of the tube leading from the main bulb is fitted with a glass tap, $K$, of fairly wide bore and very well fitting. To fill the regulator mercury is poured into the U-tube so that its level is about half-way up the capillary tube; the toluene is then placed in the bulb; electrical terminals are provided by the platinum wire dipping into the capillary and by a copper wire dipping into the other arm of the U-tube. These electrodes are connected with a small relay which cuts out or inserts the resistance $R_2$ in the circuit. Adjustment is effected by bringing the bath to the required temperature with the tap, $K$, open. The tap is then closed and the electrode tip adjusted to the surface of the mercury in the capillary. This regulator works extremely well, and with a bath of 27 litres it is capable of keeping the temperature constant to 0·02° at 25°. Calculations are given to show how the values of $R_1$ and $R_2$ may be arrived at for any particular temperature. J. F. S.

**The Specific Heats of some Sulphides Used in Metallurgy, with Special Reference to High Temperatures.** K. BORNEMANN and O. HENGSTENBERG (*Mitt. Metallhütt. Inst. Tech. Hochschule Breslau*, 1920, 18 pp.).—By means of Oberhoffer's vacuum method improved by substituting a Nernst metal calorimeter for the Bunsen ice calorimeter, the specific heats of the quartz used as container and of several sulphides were determined. The figures for quartz (to 1400°) agree best with those of Magnus (A., 1913, ii, 103) but also satisfactorily with those of White (A., 1909, ii, 966) and of Wüst. Results at 100° intervals given in tabular and graphic form can be summarised as follows: galena, 0—600°, 0·0500—0·0540; cuprous sulphide, 0—900°, 0·1432—0·1369; iron sulphide, 0—1200°, 0·1664—0·2216 (heat of fusion calculated as 60 cal. per gram); magnetic pyrites, 0—100°, 0·1531; pyrites, 0—100°, 0·1284; zinc blende, 0—900°, 0·1249—0·1351; Emser blende,

0—900°, 0·1187—0·1311; Annam blende, 0—900°, 0·1131—0·1287. In zinc blendes containing much iron the relation between temperature and the average specific heats suggests a reciprocal solubility of ferrous sulphide and zinc sulphide at high temperatures. Between 720° and 760° the iron-zinc blendes showed two transition points not thus far known and these were confirmed by thermal analysis. CHEMICAL ABSTRACTS.

**The Energy of Gaseous Molecules.** J. R. PARTINGTON (*Trans. Faraday Soc.*, 1922, **17**, 734—741).—The experimental values of the molecular heats at constant volume of various monatomic, diatomic, and polyatomic gases are critically reviewed in the light of the equipartition of energy theory. It is suggested that exchange of energy in molecular collisions may occur in quanta, the energy being likewise distributed among the various degrees of freedom. The author discusses the translational energy of gaseous molecules, when the frequency in the energy quantum relation $\varepsilon = h\nu$ is identified with the mean value of the collision frequency. It is suggested that although the translational energy is almost exactly equal to the equipartition value, at the ordinary temperature, the rotational energy may depend on the former through a whole-multiple relation existing between the respective frequencies. Vibrational frequencies are, as in the case of solid bodies, assumed to be independent of temperature. The values, deduced from experimental data, of the internal molecular heat of hydrogen at various temperatures, are compared with theoretical values calculated by means of the formulæ given respectively by Einstein, Nernst and Lindemann, Nernst, and an empirical formula of the author, in the form $\beta\nu' = 6541/\sqrt{T}$, where $\nu'$ is the rotational frequency, equal to 1000 $\nu$, where $\nu$ is the translational frequency. The energy of the hydrogen and nitrogen molecules is considered from the point of view of Bohr's theory of atomic structure, as developed by Krüger (*Ann. Physik*, 1916, **50**, 346; **51**, 450). The theory indicates the molecular heat of nitrogen to be higher than that of hydrogen and less affected by temperature. J. S. G. T.

**Melting Interval of certain Undercooled Liquids. The Use of Liquid Air as a Refrigerant.** JOHN BRIGHT FERGUSON (*J. Physical Chem.*, 1922, **26**, 549—552).—It has been previously noted by McIntosh and Edson (A., 1916, ii, 230) that solids formed by the sudden chilling of aqueous solutions of salts and acids do not show a melting interval extending from the eutectic point to the temperature at which such a liquid solution would be in equilibrium with a trace of pure ice, but rather melted exactly at this temperature. These authors prepared constant temperature baths by using such chilled materials. The present author has prepared and investigated a number of such chilled materials (glasses) from solutions of sodium chloride and hydrochloric acid. It is shown that the constant temperatures obtained on melting the ...s are dependent on the particular experimental conditions.

In the case of salt solution glasses, these temperatures approach the liquidus temperature, but are always below it. The analysis of the residual slushes left on partial melting indicate that the salt solution glasses may persist for some time at temperatures above the liquidus temperature. Since there does not appear to be an exact relation between the melting temperatures and the liquidus temperatures, the use of such glasses for constant temperature baths cannot be regarded as of general application. One explanation of the constant temperature obtained with these glasses is that this temperature is the point at which the heat absorbed by the melting glass exactly equals the heat of partial crystallisation of the excess component together with the heat lost through the walls of the container. The heat given out when unit weight of the excess component crystallises is probably very great when compared with the heat absorbed when unit weight of the glass melts. If the glass melts slowly, a constant temperature would result which would be near the liquidus temperature, but, on the other hand, if the glass melts quickly the constant temperature would be considerably below the liquidus temperature. When liquid air is used to "freeze" a solution, it is shown that the true melting curve may be obscured by the presence of the glass in the melting mass. J. F. S.

**Vapour Pressures and Heats of Vaporisation of Non-associated Liquids.** F. SPENCER MORTIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1429—1435).—A theoretical paper in which empirical methods for evaluating the constants in the vapour pressure and sublimation pressure equations: $\log P_v = C_v - S_v/T$ and $\log P_s = C_s - S_s/T$ are given and their significance is discussed. It is shown that $S_v$, the slope of the $\log P vs. 1/T$ curves is, for normal liquids, given by the expression $S_v = -68 + 4{\cdot}877T_b + 0{\cdot}0005T_b^2$. It is demonstrated from existing experimental data that the molecular heat of vaporisation is equal to $4{\cdot}23S_v$ rather than $4{\cdot}58S_v$, the value generally adopted. It is shown that the values of the molecular latent heats of vaporisation calculated from the equation $L_v = 4{\cdot}23S_v$ are generally in better agreement with the experimental results than those calculated from the equations put forward by Trouton, Bingham, or Nernst. This advantage is especially noticeable when the equations are applied to substances boiling at high temperatures. Thus in the case of cadmium $T_b = 1057°$, $L_{obs.} = 23480$, $L_{calc.} = 4{\cdot}58S = 26300$, $L_{calc.} = 4{\cdot}23S = 23920$; (Trouton) 22720; (Bingham) 30200; (Nernst) 22550. The thermodynamical equations connecting heats of vaporisation, heats of sublimation and heats of fusion and the relationships with vapour pressure and sublimation pressure are briefly reviewed and empirical methods for calculating each from the freezing and boiling points are put forward for normal liquids. J. F. S.

**The Heat of Formation of Aluminium Nitride.** FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1922, **5**, 448—454).—The aluminium nitride used for the experiments was prepared from aluminium bronze and contained about 91% of AlN and 0·5%

of silicon, the remainder being alumina. The heat of combustion was measured in a bomb calorimeter, the nitride being mixed with a proportion of benzoic acid to facilitate combustion. The heat of combustion found for the reaction $2AlN+3O=Al_2O_3+N_2$ was 258·2 (254·8) Cal. Substracting this from the heat of combustion of aluminium, $2Al+3O=Al_2O_3+380{\cdot}2$ Cal., the value for the heat of formation of aluminium nitride is $Al+N=AlN+61{\cdot}0$ (62·7) Cal. The figure in brackets is the corrected value, assuming that all the silicon present in the nitride was in the elementary form. The value found is considerably higher than that obtained by previous workers, 55—56 Cal. E. H. R.

**The Graphitic Conception of Aromatic Carbon.** A. L. von Steiger (*Ber.*, 1922, **55**, [*B*], 1968—1979).—It has been shown previously that the heats of combustion of aromatic hydrocarbons can be calculated on the assumption that all aromatic C–C and C–H linkings are equivalent but differ from the corresponding aliphatic linkings. The value for the aromatic C–C linking which is thus deduced agrees very closely with that of the graphite main linking and thus important evidence of the graphitic conception of aromatic carbon, as postulated by Debye and Scherrer, is adduced. Attempts to apply similar methods to the calculation of molecular refractions have also been described (A., 1921, ii, 473), and it has been found that the results, based on linking constants, harmonise better with the observed values than do those calculated by Brühl's summation method. These results have been criticised adversely by von Auwers (this vol., ii, 98), who has pointed out that an incorrect value has been adopted for the molecular refraction of naphthalene; this is admitted, but it is pointed out that, although the deviation from strict additivity is thereby rendered more pronounced, the superiority of the newer method of calculation still remains.

The molecular refractions of the alkylbenzenes have been examined. With a compound such as ethylbenzene, the summation for the phenyl group is effected with aromatic, that of the ethyl radicle with aliphatic, constants; the character of the C–C linking joining the two halves of the molecule remains undecided, but is assumed provisionally to be of an aliphatic nature. The agreement between the calculated and observed values for the lower benzene homologues is very satisfactory; with the methyl compounds, depressions are observed which become more marked as the methyl groups are in closer proximity to one another and thus attain their maximum in compounds such as 1 : 2 : 3 : 4-tetramethylbenzene.

The communication concludes with a reply to the criticisms of Wibaut (this vol., ii, 239) and von Weinberg (A., 1921, ii, 668, 669). H. W.

**The Heat of Combustion of Benzoic Acid, Cane-sugar, and Naphthalene.** W. Swientoslawski and [Mlle] H. Starczewska (*Bull. Soc. chim.*, 1922, [iv], **33**, 654—667).—A survey of previous work on the subject reveals discrepancies between the

results obtained by various workers (cf. Wrede, A., 1910, ii, 1038; Roth, A., 1910, ii, 584; Swientosławski, A., 1915, ii, 315, and 1921 ii, 679; Dickinson, *Bull. Bur. Stand.*, 1915, **11**, 190; Richards, A., 1920, ii, 589; Jessy, this vol., ii, 1041; Henning, A., 1921, ii, 379; Verkade, this vol., ii, 474). Further measurements made by the authors are here compared with those of Dickinson and Verkade, and the opinions expressed by the latter (*loc. cit.*) as to the advisability of choosing benzoic acid as the standard substance are now supported by fresh experimental evidence. Reference is made to the consideration of this subject by the International Conference of Pure and Applied Chemistry, Lyons, 1922.

H. J. E.

**Heat Developed on Mixing Sulphuric Acid, Nitric Acid, and Water.** J. W. McDavid (*J. Soc. Chem. Ind.*, 1922, **41**, 246—250T).—The heat developed on mixing various proportions of the following pairs of substances: 49·2% nitric acid and 96·16% sulphuric acid, 20·0% nitric acid and 96·16% sulphuric acid, 96·8% nitric acid and 60·0% sulphuric acid, 96·8% nitric acid and 99·5% sulphuric acid, and a mixed acid containing 49·8% sulphuric acid, 48·4% nitric acid, and 1·8% water with water, has been determined calorimetrically. From the results obtained together with Thomsen's values for the heat of dilution of sulphuric and nitric acids respectively ("Thermochemistry," Thomsen, Burke, p. 76), triangular diagrams have been constructed whereby the heat developed on making any mixture of the three substances may be obtained. J. F. S.

**Compressibility of Exhausted Flasks in the Determinations of the Densities of Gases.** E. Moles and R. Miravalles (*Anal. Fís. Quím.*, 1922, **20**, 104—116).—The contraction of flasks used in the determinations of gas densities due to atmospheric pressure may be expressed by the empirical formula $x=17{\cdot}5\,.\,V/W\times 10^{-6}$, where $x$ is the contraction per litre of volume, $V$ the volume of the flask, and $W$ its weight. Measurements made on six flasks by three methods showed good agreement of observed values with values calculated from the formula. G. W. R.

**The Compressibility at 0° and less than 1 Atmosphere and the Divergence from Avogadro's Law of Several Gases.** Ph. A. Guye and T. Batuecas (*Helv. Chim. Acta*, 1922, **5**, 532—543).—To determine accurately the molecular weight of a gas by physico-chemical methods, it is necessary to know accurately the weight of a normal litre, $L_0$, of the gas and its divergence from Avogadro's law, $1+\lambda$. A method is described for measuring with great precision the compressibility of a gas at 0°, from which $1+\lambda$ can be calculated. The apparatus consisted of three cylindrical glass bulbs of approximately equal volume, accurately calibrated, in a vertical column, connected together by capillary tubing and at the top communicating with a barometer. The volume of the gas was measured in this apparatus at approximately 1, $\frac{1}{2}$, and $\frac{1}{3}$ atmosphere. Experiments were made with oxygen, hydrogen,

and carbon dioxide. The divergence from Avogadro's law was calculated from the formula $1+\lambda=(pv)_0/(pv)_1$ (cf. Guye, A., 1919, ii, 318).

The oxygen used was prepared by three different methods, from potassium permanganate, from a mixture of sodium and potassium chlorates, and electrolytically. The mean value obtained for $1+\lambda$ was $1{\cdot}00085 \pm 0{\cdot}00002$, and the coefficient of compressibility per cm. is $11{\cdot}3 \times 10^{-6}$. Taking $L_0=1{\cdot}42891$, the value of the gas constant $R$ is 22·414. Hydrogen was prepared by the action of concentrated potassium hydroxide on aluminium and also electrolytically. The mean value found for $1+\lambda$ was $0{\cdot}99935 \pm 0{\cdot}00002$, which, taking $L_0=0{\cdot}089858$, gives for the atomic weight of hydrogen 1·0077. The coefficient of compressibility is $-8{\cdot}6 \times 10^{-6}$. Carbon dioxide was prepared by heating pure sodium hydrogen carbonate and by the combustion of sucrose. The mean value of $1+\lambda$ was $1{\cdot}00706 \pm 0{\cdot}00004$; taking $L_0=1{\cdot}97685$, this gives as the atomic weight of carbon 11·998, somewhat less than the value accepted by the International Committee, 12·05, but in good agreement with the probable correct value 12·00. The coefficient of compressibility is $92{\cdot}2 \times 10^{-6}$. E. H. R.

**The Compressibility at 0° and less than 1 Atmosphere and the Divergence from Avogadro's Law of Several Gases. II. Ethylene.** T. BATUECAS (*Helv. Chim. Acta*, 1922, **5**, 544—546; cf. preceding abstract).—Ethylene was prepared by the action of sulphuric acid on ethyl alcohol and by the catalytic action of heated alumina on ethyl alcohol vapour. The mean value found for $1+\lambda$ was $1{\cdot}00780 \pm 0{\cdot}00004$; taking $L_0=1{\cdot}26401$, the molecular weight is found to be 28·032, and the atomic weight of carbon 12·000. The coefficient of compressibility is $102 \times 10^{-6}$.

E. H. R.

**Measurement of Surface Tension.** ROBERT B. ELDER (*J. Physical Chem.*, 1922, **26**, 558—562).—A theoretical paper in which the author discusses the measurement of surface tension in connexion with the work of Ferguson (A., 1914, ii, 768) and of Bhatnagar (A., 1921, ii, 169). It is shown that although the numerical values of the latter author are very close to those of Ferguson, the method used involves a number of errors which are partly compensating. The method and errors are discussed.

J. F. S.

**Method for the Determination of the Surface of Adsorbing Powders.** FRITZ PANETH and WALTER VORWERK (*Z. physikal. Chem.*, 1922, **101**, 445—479).—The authors have put forward a rapid and trustworthy method for determining the surface of an adsorbing powder. The method is based on the following considerations. When a sparingly soluble powder is shaken with its saturated solution there will be an exchange of molecules between the surface of the powder and the solution; if it were possible to identify the molecules of the substance in solution, or at least a portion of them, then the partition of these between the solution

and surface could be determined, and at equilibrium the ratio of the identified molecules on the surface to the identified molecules in solution will be equal to the ratio of the total molecules on the surface to the total molecules in solution. This process can be actually carried out for substances which have isotopes; thus in the case of lead sulphate, thorium-*B* can be used and will constitute the identified molecules. The process can be followed by an electroscope and represented by the equation Isotope(ads)/Isotope(sol)=Element(surf)/Element(sol). The ratio of the isotope adsorbed to the isotope in solution can be determined from the change in the $\beta$-ray activity of the solution, and the amount of lead in solution can be determined by analysis, hence, Element(surf), that is, the weight of the surface layer, can be calculated. Using this method, the weight of the surface layer of one gram of various specimens of lead sulphate and lead chromate has been determined. The values obtained in grams of lead per gram of material are: lead sulphate $6{\cdot}4\times10^{-4}$ and lead chromate $69{\cdot}2\times10^{-4}$. These values have been controlled by microscopic examination and found to be somewhat larger than the microscopic values, but of the same dimensions. J. F. S.

**Thickness of the Adsorbed Layer in the Adsorption of Dyes by Crystals.** FRITZ PANETH and WALTER VORWERK (*Z. physikal. Chem.*, 1922, **101**, 480—488).—The adsorption of ponceau-2R by lead sulphate has been determined and from the amount adsorbed and the dimensions of the surface of the lead sulphate (cf. preceding abstract), it is shown that the adsorbed layer is one molecule thick. J. F. S.

**The Sorption of Carbonyl Chloride by Beechwood Charcoal.** HUGH MILLS BUNBURY (T., 1922, **121**, 1525—1528).

**The Relation between Adsorption and Electrolytic Dissociation.** M. A. RAKUSIN (*Biochem. Z.*, 1922, **130**, 282—285).—When a porous pot is immersed in solutions of sucrose or sodium chloride, the concentration of the solution increases owing to negative adsorption. This is correlated with the general adsorption of colloids and non-adsorption of electrolytes. H. K.

**Chemical Adsorption.** G. STADNIKOFF (*Kolloid Z.*, 1922, **31**, 19—32).—The author differentiates four types of adsorption: (1) solution adsorption, which is represented by Henry's law, $c_2=kc_1$; (2) chemical adsorption, represented by the equation $c_2=\sigma c_1/(1+\sigma_1c_1)$; (3) combined adsorption, represented by the equation $c_2=kc_1+\sigma c_1/(1+\sigma_1c_1)$, and (4) exchange adsorption, represented by $(mc_2 \,.\, c'_1v)/(mc'_2 \,.\, c_1v)=k$; or $c_2c'_1/c'_2c_1=k$. The author is of the opinion that chemical adsorption can only be definitely proved in the case of an adsorbent of definite composition possessing either marked acid or basic properties, adsorbing either base or acid from solution. With the object of ascertaining whether or no a chemical explanation for adsorption is possible, the adsorption of sulphuric, hydrochloric, nitric, and acetic acids and mixtures of two of these acids and also of iodine by aniline-black, prepared both

by the use of potassium dichromate and of potassium persulphat has been investigated. In the case of sulphuric acid, the maximur adsorption is two molecules of sulphuric acid to one of anilin black, and the adsorption is entirely reversible. The limiting valu of the adsorption of hydrochloric acid is three molecules of hydrc chloric acid to one molecule of aniline-black and in this case th formula for chemical adsorption is fully followed. The limitin adsorption of acetic acid is two molecules of the acid to one of th adsorbent, whilst in the case of the adsorption of iodine, twelv iodine atoms are adsorbed to each molecule of aniline-black, that i two iodine atoms to each quinonoid nitrogen atom of the tri-quinonoi aniline-black. The experimental results of other authors have bee recalculated from the point of view of chemical adsorption (c Willstätter and Dorogi, A., 1909, i, 535, 975). J. F. S.

**Dissociation of Hydrogen in a Tungsten Furnace an Low Voltage Arcs in Monatomic Gases.** O. S. DUFFENBAC (*Science*, 1922, **55**, 210—211).—A furnace consisting of a cylinde of thin sheet tungsten, and an axial tungsten filament, both heate electrically, was used to determine the voltages at which the ar was struck and broken. The results were in agreement with thos required by Bohr's theory for the ionising (13·52 volts) and radiatin (10·14 volts) potentials of the hydrogen atom, and the potenti (16·4 volts) which, according to Bohr's theory, is approximatel that necessary to accelerate an electron so that it will dissociat the molecule and ionise one of the atoms on impact. Calculate values for the percentage of monatomic hydrogen in equilibriur with diatomic hydrogen at temperatures from 1000° *K*. to 3000° *K* appeared to be confirmed by the experimental results. A. A. E.

**Formation and Dissociation of some Polyhalogen Com pounds of Hydrogen in Aqueous Solution.** PRIYADARANJA RÂY and PULIN VIHARA SARKAR (T., 1922, **121**, 1449—1455).

**Dissociation of Glucinum Sulphate.** (MLLE) G. MARCHA (*Compt. rend.*, 1922, **175**, 270—272).—Glucinum sulphate decompose under the influence of heat according to the equations $GlSO_4 = GlO + SO_3$, and $2SO_3 \rightleftharpoons 2SO_2 + O_2$, and the total equilibrium pressur corresponding with temperatures from 590—830° was measured b means of a mercury manometer, the anhydrous sulphate being heate in an electric furnace in a previously exhausted porcelain tube, an the temperature measured with a le Chatelier platinum-rhodiun couple. Utilising the known equation for the equilibrium o dissociation of sulphur trioxide, the partial pressures of sulphu trioxide, sulphur dioxide, and oxygen were calculated from th data obtained. The complete results are recorded in tabular forn and include the following values for the partial pressures of sulphu trioxide, sulphur dioxide, and oxygen, respectively: at 700°, 3·30 6·34, and 3·17 cm.; at 750°, 9·12, 18·24, and 9·12 cm., and at 785° 17·23, 35·58, and 17·79 cm. Utilising the pressures at the abov temperatures, the equilibrium equation was found to be $\log p_{SO_3} = -14907/T - 14{\cdot}1 \log T + 57{\cdot}97$, and the results obtained for othe

temperatures from this equation agreed well with the pressure actually observed. The heat of dissociation of glucinum sulphat was calculated to be −53·5 cal. by comparison with that of coppe sulphate and its decomposition pressures as determined by Plüdde mann (*Diss.*, Berlin, 1907). G. F. M.

**Thermostat Arrangement for the Determination of th Effect of Temperature on Diffusion.** L. W. Öholm (*Hyllnings skrift tillägnad Ossian Aschan*, 1920, 9—17).—Experiments wer carried out with potassium chloride and sugar solution (0·25*N* 0·5*N*, and *N*) in a rectangular copper vessel with glass sides, i which the circulation was maintained by a propeller driven b an electric motor supported so as to prevent any shaking of th thermostat; the temperature was constant to ±0·15°. In th equation $\alpha=A+B \log k$, where $\alpha$ is the temperature coefficient $A$ and $B$ are constants, and $k$ is the diffusion coefficient, $\alpha$ fo potassium chloride between 13·5° and 29·5° was found to have a average value of 0·025, and for sugar between 13·7° and 28·7° th average value was 0·033. Chemical Abstracts.

**The Determination of Molecular Weight by means o Osmotic Pressure.** Foix (*Bull. Soc. chim.*, 1922, [iv], **33**, 653—654).—The author has measured osmotic pressures without usin semi-permeable membranes in order to eliminate errors due t imperfections in the membrane. A solution is placed togethe with pure solvent in a closed system at constant temperature. I the weight of the solution remains constant, the distance betwee the free surfaces of the two liquids will be equal to the height o the corresponding osmotic column, since, for a perfect osmomete *in a closed space, when equilibrium is reached the vapour shoul* be in equilibrium both with the surface of the solution at the to of the column and with the pure solvent at its base. It is claime that the method is successful, although it is difficult to maintai constant temperatures over the long period of time required t effect the measurement. H. J. E.

**Solubility of Gases in Liquids.** B. S. Neuhausen (*J Physical Chem.*, 1922, **26**, 553—557).—The author has plotted th solubility data for ammonia, hydrogen chloride, sulphur dioxide and carbon dioxide in methyl alcohol and ethyl alcohol and fron the results shows that the formula $V=K(P\sigma/P_0)^{1/n}$ is applicable t the solubility of these gases in the solvents named, as was previousl (this vol., ii, 264) shown for aqueous solutions. The values of th constants $K$ and $1/n$ are given for all three solvents. J. F. S.

**Melting Point, Latent Heat of Fusion, and Solubility** F. Spencer Mortimer (*J. Amer. Chem. Soc.*, 1922, **44**, 1416—1429).—A theoretical paper in which a method of calculating th solubility of substances forming non-ideal solutions is described It is shown that for those systems which do not form molecula complexes or solid solutions the ratio of the experimental to th ideal slope of the log *N vs* . $1/T$ curves is a factor which may b determined by a graphical method. Three methods are describe

whereby the ideal slope of the log *Nvs* . $1/T$ curves for any solute may be found. It is pointed out that the solubility or melting-point method of determining the latent heat of fusion of organic compounds gives very accurate results when interpreted in the light of the principles laid down in the paper. Some generalisations in connexion with the nature of binary systems obtained with various types of mixtures are put forward. The uses of these principles in determining the choice of a solvent for crystallisations and molecular-weight determinations are suggested. J. F. S.

**Reactions in Fused Salt Media. II. Solvolysis.** J. F. G. HICKS and WALLACE A. CRAIG (*J. Physical Chem.*, 1922, **26**, 563—576; cf. this vol., ii, 147).—The authors have investigated the reactions which occur when lead chromate, lead oxide, silver chromate, and barium chromate, respectively, are dissolved in molten sodium chloride and in an equimolecular mixture of sodium and potassium nitrates at various temperatures up to about 850°. For comparative purposes the hydrolysis of lead chromate in water has been investigated both at ordinary pressure and under increased pressure. It is shown that the solvolysis of lead, silver, and barium chromates by a fused equimolecular mixture of sodium and potassium nitrates represents states of equilibrium analogous to hydrolysis. Of these reactions, the solvolysis of lead chromate is the most complete and that of silver chromate the least complete. The regularity with which the constants of solvolysis vary between consecutive observations follows the same order, and the marked irregularity in the case of silver chromate suggests the possibility of another factor entering into the reaction. The solvolysis of lead chromate by fused sodium chloride also represents a true state of equilibrium, whilst in the case of silver chromate the reaction goes to completion. In the solvolytic reactions studied, equilibrium is reached in about one hundred minutes, and the constants of solvolysis may be calculated with a fair degree of accuracy. The solvolysis of lead oxide by fused sodium chloride proceeds to completion at 850—870°, and that of silver chromate is also complete at the same temperature, but here the reaction occurs much more rapidly. The present work indicates that lead chromate and litharge combine by simple molecular addition after part of the former has undergone solvolysis in the nitrate flux. In other words, the red basic lead chromates are higher order compounds. The relatively small degree of solvolysis of lead chromate and the practically complete solvolysis of lead oxide by the same reagent under the same conditions explains the failure to obtain red basic lead chromates when a fusion containing lead chromate, lead oxide, and sodium chloride is rapidly cooled, and also the appearance of the red basic lead chromates when a similar fusion is slowly cooled. The results confirm the assumption of the dissociation $Pb_2CrO_5 \rightleftharpoons PbO + PbCrO_4$. This assumption was previously (*loc. cit.*) offered as an explanation of the failure to obtain red basic lead chromates when a fusion containing lead oxide, lead chromate, and sodium chloride was poured into water and agrees well with the evidence offered by

the thermal equilibrium diagram plotted for the system lead chromate–lead oxide. J. F. S.

**Theory of Recrystallisation.** H. ALTERTHUM (*Z. Elektrochem.*, 1922, **28**, 347—356).—The present views of recrystallisation are considered and nucleus formation and growth are regarded as a consequence of a thermodynamic instability. It is shown that the energy changes which accompany the cold working of a metallic crystal may be divided into reversible and irreversible changes, and the different degrees of working as a continuous series of different modifications. On the basis of Boltzmann's theory of probability, a formula is developed which expresses the number of nuclei of a recrystallised metal as a function of the temperature and the degree of working, which is in excellent agreement with the experimental results of Czochralski (A., 1917, ii, 302). From the same point of view, a continuous series of modifications, which differ in the degree of dispersity, is assumed and a similar formula is derived for the number of nuclei in recrystallisation by absorption of other crystals. The proportionality factors are attributed, in part, to causes which are not thermodynamic, and the possible changes of these during the process of recrystallisation are discussed. J. F. S.

**Loosening of Crystal Lattices.** G. VON HEVESY (*Z. physikal. Chem.*, 1922, **101**, 337—352).—The transport of material, that is, diffusion and electrolytic transport, in crystals is rendered possible by the gradual loosening of the crystal lattice by an increase of temperature. As a measure of the loosening tendency of a crystal, the dimensions of the change in electrical conductivity between solid and liquid at the melting point serve as the most suitable standard. This value is extraordinarily divergent for different substances, varying relatively from 1 for silver iodide to 20,000 for sodium nitrate. A close relationship exists between the loosening tendency and the electro-affinity of the ions which form the crystal. The greater the work necessary to convert the ions of a crystal into the neutral condition, the smaller is the tendency of the lattice to loosen. From this it follows that the loosening of the lattice is brought about by a disturbance of the normal condition of individual ions constituting the crystal. The increase in electrical conductivity which solid electrolytes undergo when illuminated is regarded as due to a loosening of the lattice which increases the mobility of the ions already present in the electrolyte, and the transport of electricity by electrons is regarded as a limiting case of this phenomenon. The relationship between the loosening and the overstepping of the Dulong and Petit value of the atomic heat at higher temperatures is discussed and the overstepping regarded as a preliminary condition of the melting process. J. F. S.

**Röntgenographic Determination of Crystal Arrangement.** M. POLÁNYI (*Naturwiss.*, 1922, **10**, 411—416).—Röntgenographic methods must be employed to determine whether a crystal lattice is changed by elongation of a single crystal. By means of a fila-

ment diagram it was found that for a zinc crystal (1) the lattice changes its orientation with respect to the longitudinal axis when elongated; (2) in the section drawn out to a flat band (cf. Schiebold, *Z. Physik*, 1922, **9**, 180; Carpenter and Elam, this vol., ii, 69; Gomperz, *Z. Physik*, 1922, **8**, 184) the angle that the hexagonal axis of the crystal lattice makes with the longitudinal axis changes from 10° to 18°, and (3) the cylindrical filaments resulting from further elongation of the flat bands have the same orientation of their lattices as the flat bands. It is maintained that this same kind of shift in the orientation of the lattice occurs in a zinc wire as in the individual crystal. CHEMICAL ABSTRACTS.

**Graphical Determination of Hexagonal and Tetragonal Crystal Structures from *X*-Ray Data.** ALBERT W. HULL and WHEELER P. DAVEY (*Physical Rev.*, 1921, **17**, 549—570).—A graphical method of interpreting *X*-ray patterns of powders is described, for each type of lattice the logarithms of the theoretical spacings of the different planes being plotted as functions of the axial ratio. A number of graphs are reproduced for comparison with observed spacings. Three specific arrangements have been given for each system, namely, simple prism, centred, and face-centred arrangements in the cubic and tetragonal systems, and simple prism, close packed, and rhombohedral arrangements in the hexagonal system. Since (1) all possible arrangements of atoms in the cubic, tetragonal, or hexagonal systems may be obtained by the combination of one or more identical simple space lattices of cubes, right tetragonal prisms, and right 60° triangular prisms, respectively, and (2) the intermeshing of two or more identical lattices weakens or causes to disappear some of the lines due to a single lattice, but can add no new lines, it follows that the above, and all other possible arrangements, are obtained from the simple tetragonal and triangular prism lattices, respectively, by simply omitting part of the lines. The cubic forms may be found on either the tetragonal or hexagonal plots, whilst for the orthorhombic, monoclinic, and triclinic systems the relative crystal spacings must be expressed as a function of two, three, and five variables, respectively; a simple approximate method is, however, indicated.

Zinc is shown to be a hexagonal close-packed assemblage of prolate spheroids, with axial ratio 1·860 and the side of the unit triangle 2·760 Å. Cadmium has a similar structure, the corresponding measurements being 1·89 and 2·980. Indium has a structure very similar to that of aluminium (cubic close-packed), namely, a tetragonal close-packed arrangement of prolate spheroids, with axial ratio 1·06 and a unit square of side 4·58 Å. A. A. E.

***X*-Ray Crystal Analysis of Metals.** ALBERT W. HULL (*Physical Rev.*, 1921, **17**, 571—588; cf. *ibid.*, 1917, **10**, 661; *Proc. Amer. Inst. Elec. Eng.*, 1919, **38**, 1171; A., 1919, ii, 470; 1920, [illegible], 546; 1921, ii, 38, and preceding abstract).—The crystal structure of thirteen common metals has been determined. The lattices onta-[illegible]omium, molybdenum, and tantalum are body-centred cubes oured [illegible]es 2·895, 3·143, and 3·272 Å., respectively; cobalt (α form),

nickel, rhodium, palladium, iridium, and platinum have face-centred cubic lattices with sides of cubes 3·554, 3·540, 3·820, 3·950, 3·805, and 3·930 Å., respectively; cobalt (β form), zinc, cadmium, and ruthenium have hexagonal lattices of the close-packed type with axial ratios 1·63, 1·86, 1·89, and 1·59, respectively, and with triangular sides 2·514, 2·670, 2·960, and 2·686 Å., respectively; indium has a face-centred tetragonal lattice with axial ratio 1·06 and side of elementary prism 4·58 Å. The structures of cadmium, zinc, and indium are close-packed arrangements of solid prolate spheroids, whilst that of ruthenium is a close-packed arrangement of oblate spheroids. A. A. E.

**Coagulation of Colloids.** ARNE WESTGREN and JOSEF REITSTÖTTER (*J. Physical Chem.*, 1922, **26**, 537—548).—A theoretical paper in which the authors summarise Smoluchowski's kinetic hypothesis of coagulation (A., 1917, ii, 297) and give an account of the work which has been published with the object of substantiating this hypothesis. J. F. S.

**Protecting Colloids. XII. Gelatin as Protecting Colloid. II. Colloidal Selenium.** A. GUTBIER and R. EMSLANDER (*Kolloid Z.*, 1922, **31**, 33—36; cf. A., 1921, ii, 693; this vol., ii, 142, 283, 485).—The stabilising action of gelatin on colloidal solutions of selenium has been investigated. A very stable selenium sol may be prepared by dissolving 2—3 grams of selenium dioxide in a litre of 0·1% gelatin solution made up in chloroform water and slowly reducing at 18—25° with a solution of hydrazine hydrate (1 : 1000), taking care that the reduction is stopped before the last of the dioxide is reduced. The solution is then dialysed and preserved under a layer of chloroform. The solution is red in colour, quite clear and very stable at ordinary temperatures, but on heating a red, amorphous precipitate separates. Sols prepared as above have been preserved without change for eight years. The addition of hydrochloric acid or sodium hydroxide in small concentrations to the protected colloid causes the system to be more stable to freezing than the protected colloid without the addition of electrolyte. Sodium chloride causes the solutions to change to a lighter colour, but exerts no further action on the protected colloid. The colour change is attributed to the formation of a stable complex, salt–glutin–selenium. J. F. S.

**An Inhibition Period in the Separation of an Emulsion.** T. C. NUGENT (*Trans. Faraday Soc.*, 1922, **17**, 703—707).—The author has investigated the de-emulsifying action of sodium hydroxide solution on emulsions of benzene in water, containing 50% by volume of benzene and not less than 0·1% of gelatin as stabiliser. If sodium hydroxide is added immediately after production of the emulsion, de-emulsification commences at once. If the emulsion is left undisturbed for some time prior to adding the sodium hydroxide solution, de-emulsification is inhibited for a period following such addition. The inhibition period depends on the interval between the production of the emulsion and the addition of the sodium hydroxide

solution. It is suggested that the stability of the emulsion increases with its age owing to the gradual formation of protective layers of the stabilising agent about the benzene particles. J. S. G. T.

**Precipitation of Metals by Hydrogen Sulphide.** G. McP. Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 1500—1502).—A theoretical paper in which the author suggests that should it be thought best to regard the formation of sulphide precipitates from the ionic point of view alone, then the hydrogen sulphide (HS′)-ion should be regarded as the active participating ion, and not the sulphide (S″)-ion. In support of this statement, it is shown that a $0\cdot2N$-solution of hydrochloric acid containing $0\cdot2N$-hydrogen sulphide contains in 5 c.c., $3\times10^{20}$ non-ionised molecules of hydrogen sulphide, $15\times10^{13}$ hydrogen sulphide ions, and only one sulphide ion. A further extreme case due to Knox (A., 1908, ii, 830) is considered; according to this author, mercuric sulphide has a solubility product $2\cdot8\times10^{-54}$, from which it follows that the maximum concentration of mercuric and sulphide ions is $1\cdot7\times10^{-27}$ in a saturated solution of mercuric sulphide, that is, one individual mercuric or sulphide ion in 1000 litres of solution, which implies that to maintain anything like equilibrium these ions must move with the velocity of light, a condition which is not fulfilled. J. F. S.

**Force of Adhesion in Solutions. III. Partition of Substances between two Solvents.** Nikolai Schilov, Lidie Lepin, Marie Jantschak, and Michael Dubinin (*Z. physikal. Chem.*, 1922, **101**, 353—402; cf. this vol., ii, 350).—A very large number of partition coefficients have been determined at temperatures ranging from 10° to 40°. These include: formic acid, acetic, propionic, succinic, benzoic, oxalic, tartaric, and nitric acids between ethyl ether and water; acetic, propionic, *iso*butyric, benzoic, mandelic, salicylic, trichloroacetic, and trichlorobutyric acids between benzene and water; iodine, pyridine, benzoic, and picric acids between toluene and water; benzoic and acetic acids between xylene and water; iodine, acetic, propionic, *iso*butyric, benzoic, and salicylic acids between chloroform and water; mandelic and benzoic acids between anisole and water; benzoic acid between phenetole and water; succinic acid between amyl ether and water; benzoic acid between light petroleum and water, and trichloroacetic and trichlorobutyric acids between amylene and water. It is shown that because of the mutual influence on solubility the use of the Henry–Dalton law, in connexion with the partition of substances between two liquid phases, is extremely limited, and the law therefore represents an ideal limiting condition which rarely occurs. The difference between dilute and concentrated solutions is not fundamental, but only quantitative. The partition coefficient is generally dependent on the total concentration of the solute, and the constancy of this quantity cannot alone be taken as a proof of the Henry-Dalton law, because mutual compensating volume changes in the liquids can occur, as has been actually shown in the present experiments. The limiting value of the partition coefficient at large concentrations of the solute is

›t, in general, determined by the ratio of the individual solu-lities in the two solvents, but by the ratio of the concentrations the two phases at the triple point, solid–liquid–liquid. The ›rtition data are readily presented graphically if the relative ncentrations of the solute in the individual phases are plotted a function of the total concentration. In this way, for each ›rtition two coupled isotherms are obtained which in many cases ›ve characteristic forms and serve to differentiate the various pes. The partition coefficient can be expressed by the general ›proximation formula $K=C_1/C_2^n=C_1/C_2^{\log\beta_1/\log\beta_2}$, in which $\beta_1$ d $\beta_2$ are defined by the change of concentration of the individual ases brought about by definite changes in the total concentration the solute. The index *n* therefore becomes any suitable figure, d only in a few special cases has it a stoicheiometric significance. many of the cases examined now and previously the mean lues of $\beta_1$, $\beta_2$, and *n* for the region of larger concentrations are proximately constant and may be followed up to the triple int. The partition of substances which are infinitely soluble both phases is determined by the dissolving power of both ›vents with respect to the solute. The coupled isotherms are nvergent and meet at the critical mixture point of the two ases. This phenomenon can be investigated by partition and xing experiments and furnishes information about the depend-ce of the dissolving power of water and organic solvents on nstitution. Experiments on the kinetics of partition show finitely that with respect to the equilibrium concentrations rtition is a time reaction of the first order. The slow diffusion ›cess of the solute through the interface and through the con-ntrated layers which adhere to the interface is determinative of › velocity as in the case of heterogeneous systems of solid and uid. The velocity constants obtained are to a degree propor-nal to the number of rotations per minutes of the reaction ›sels and independent of the absolute amount of substance fusing. J. F. S.

**System $Na_2O$–$CO_2$–NaCl–$H_2O$, considered as two Four ›mponent Systems.** F. A. FREETH (*Phil. Trans.*, 1922, [*A*], 3, 35—87).—The solubility relations in the systems $Na_2CO_3$–›Cl–$H_2O$; $Na_2CO_3$–NaOH–$H_2O$; $Na_2CO_3$–$NaHCO_3$–$H_2O$; NaOH–›Cl–$H_2O$; $NaHCO_3$–NaCl–$H_2O$; $Na_2CO_3$–NaOH–NaCl–$H_2O$ and ›$_2CO_3$–$NaHCO_3$–NaCl–$H_2O$ have been experimentally determined 0°, 10°, 15°, 20°, 25°, 30°, 35°, 45°, and 60°. Numerous tables the results and diagrams representing the relationships are luded in the paper, from which the composition and quantity the stable phases formed from any mixture of the components ›y be deduced. J. F. S.

**Liesegang's Phenomenon and Precipitate Formation.** G. CHATTERJI and N. R. DHAR (*Kolloid Z.*, 1922, **31**, 15—16).— continuation of work previously published (this vol., ii, 205), is shown that the peptisation of insoluble hydroxides of iron, ›alt, uranium, and thorium may also be brought about by

gelatin, agar, glue, gum arabic, and starch in the manner previously employed with glycerol. In the case of peptisation by glycerol, it is shown that this is governed by the concentration of the reacting substances. Thus glycerol does not peptise ferric hydroxide in the presence of concentrated solutions of ferric chloride. The authors describe experiments to show that the formation of Liesegang rings is closely connected with the above-named actions, and that here also the concentration of the reacting solutions is an important factor. J. F. S.

**Velocity of Chemical Change in Solid Substances.** C. N. HINSHELWOOD and E. J. BOWEN (*Z. physikal. Chem.*, 1922, **101**, 504—505).—A discussion of Sieverts and Theberath's conclusions on the velocity of chemical reactions in solid systems (this vol., ii, 360), and a reference to the author's experimental work on the same subject (A., 1920, ii, 743; 1921, ii, 443; T., 1921, **119**, 721). J. F. S.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. II. Reaction of Permanganate and Formic Acid in Neutral Solution.** JOSEF HOLLUTA and NIKOLAUS WEISER (*Z. physikal. Chem.*, 1922, **101**, 489—497; cf. this vol., ii, 448).—The reduction of potassium permanganate in neutral solution by formic acid has been examined at 17° and 26·75°. It is shown that the disturbances observed in the reductions carried out in acid solution disappear in neutral solutions; these disturbances are observed down to acid concentrations 0·001*N*, and are greatest at the start of the action. The reduction in acid solutions is represented by the equations $2(MnO_4' + HCO_2' + H_2O = MnO_4'' + CO_3'' + 3H^{\cdot})$ and $2MnO_4'' + HCO_2' + 7H^{\cdot} = 2Mn(OH)_4 + CO_2$. The temperature coefficient of the reaction is 1·88, a perfectly normal value which is very close to the value observed for the action in dilute acid solutions (*loc. cit.*). J. F. S.

**Antioxidants and Antioxygenisers.** A. SEYEWETZ and P. SISLEY (*Bull. Soc. chim.*, 1922, [iv], **33**, 672—676).—A review of the subject in which reference is made to the work of Bigelow (A., 1898, ii, 506), Titoff (A., 1904, ii, 113), Lumière and Seyewetz (A., 1905, ii, 379), Sisley (*Rev. gén. mat. col.*, 1911, 337), and Moureu and Dufraisse. The suggestion is made that the term antioxygeniser (*antioxygène*) applied by the last named is less suitable than antioxidant (*antioxydant*) suggested by Lumière and Seyewetz. H. J. E.

**Catalysis with Special Reference to Newer Theories of Chemical Action. I. The Radiation Theory of Chemical Action. (1) Radiation and Chemistry.** JEAN PERRIN. **(2) The Radiation Hypothesis of Chemical Reactivity and some of its Applications.** W. C. McC. LEWIS. **(3) A Theory of Chemical Reaction and Reactivity.** E. C. C. BALY. **(4) Is a True Unimolecular Action Possible ?** T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1922, **17**, 546—572, 573—587, 588—595, 596—597).—(1) A review of the author's radio-chemical theory of reactions

("Les Atomes," 1913; A., 1919, ii, 177), which is in accord with the laws of Arrhenius and of Planck. Experimental verification of the theory is derived from a consideration of the phenomena of photochemistry, luminescence, and organic fluorescence. The theory is extended to the phenomena of radioactivity.

(2) A review of the author's application of the quantum radiation hypothesis to the investigation of the mode whereby energy necessary to produce chemical change in catalytic or non-catalytic processes is communicated to the reactant unit (cf. T., 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 796; 1918, **113**, 471; 1920, **117**, 1120).

(3) Chemical reaction between atoms is conceived as consisting in the joint loss of an equal amount of energy by the reacting atoms, whereby a stable molecule is produced. The atoms in combination retain their individuality as absorbers or radiators of energy. The least possible amount of energy that the molecule can lose is a multiple of the least common integral multiple of the frequency quanta of its component atoms. The theory is confirmed by the phenomena observed in the photochemical combination of hydrogen and chlorine, and the possibility of the existence of two samples of a gas, for example, ammonia in apparent thermal equilibrium but in different molecular phases.

(4) The author contends that none of the actions to which the radiation hypothesis has been applied involves only a single molecule. The application of the hypothesis to cases of radioactive disintegration and bombardment by α-particles, where single molecules are involved, is unnecessary. The foundation of the radiation hypothesis is consequently doubtful. J. S. G. T.

**Catalysis with Special Reference to Newer Theories of Chemical Action. II. Heterogeneous Reactions. (1) Chemical Reactions on Surfaces. (2) The Mechanism of the Catalytic Action of Platinum in the Reactions $2CO+O_2=2CO_2$, and $2H_2+O_2=2H_2O$.** IRVING LANGMUIR (*Trans. Faraday Soc.*, 1922, **17**, 607—620, 621—654).—(1) The author reviews his theory of adsorption at solid surfaces and the modus operandi of chemical reactions occurring thereat. Films adsorbed at solid surfaces are exceedingly stable, are unimolecular in thickness, and are oriented with regard to the adsorbing surface. Adsorption occurs as the result of a time lag between condensation and evaporation occurring at the surface. The orientation of the molecules on the adsorbing surface is a vital factor in determining the activity of the surface towards reacting gases. Differences in the geometrical arrangement of the atoms in the surface are responsible for the activation of catalysts effected by the action that occurs on them. Reactions between separate phases of constant composition occur only at the boundaries of phases.

(2) A detailed account is given of a theoretical and experimental investigation of the conditions determining the combination of (*a*) carbon monoxide and oxygen, and (*b*) hydrogen and oxygen, occurring at a smooth platinum surface. In the case of the former

reaction, for the range of temperatures 500—700° *K.*, the platinum surface is nearly completely covered by a unimolecular carbon monoxide film and reaction occurs only when carbon monoxide molecules strike oxygen atoms which have become adsorbed in the spaces left vacant by the evaporation of carbon monoxide molecules. For the range of temperatures 750—1050° *K.*, the surface is nearly covered with oxygen when there is an excess of oxygen, and the reaction velocity is limited by the rate at which carbon monoxide molecules strike the surface. With an excess of carbon monoxide, the surface is largely bare, and the reaction velocity is limited by the rate at which oxygen molecules strike the surface. In the case of the reaction between hydrogen and oxygen, at low temperatures (300—600° *K.*), the reaction velocity depends on the previous treatment of the platinum. With relatively inactive platinum, the results resemble those obtained with carbon monoxide and oxygen, the reaction velocity being roughly proportional to the pressure of oxygen and inversely to that of the hydrogen. At temperatures between 700° *K.* and 1900° *K.*, the results correspond closely with those obtained with carbon monoxide and oxygen. At these temperatures, the reaction is not sensitive to the previous treatment of the platinum. Adsorbed oxygen atoms are very reactive towards hydrogen, whilst under certain conditions adsorbed hydrogen atoms are relatively inactive towards oxygen molecules. J. S. G. T.

**Induced Reactions and Negative Catalysis.** N. R. Dhar and N. N. Mittra (*Trans. Faraday Soc.*, 1922, **17**, 676—680).—The phenomenon of induced reaction studied by Dhar (T., 1917, **111**, 690) is shown to be of general occurrence. Negative catalysis, due probably to the formation of intermediate compounds, occurs in oxidation reactions when the catalyst is readily oxidisable. It is concluded that one chemical change will promote or induce another chemical change of the same type. J. S. G. T.

**Adsorption and its Bearing on Catalysis.** Marcel Guichard (*Bull. Soc. chim.*, 1922, [iv], **33**, 647—653).—A study of the effect of variation of surface on catalytic activity. In the case of silica, a diagram is given showing the different amounts of water vapour adsorbed at various temperatures and constant pressure by the catalyst after preliminary heating to different temperatures; increase in the temperature of preliminary heating decreases activity in adsorption. Similar results are obtained in the case of finely divided nickel and also for various solids in respect of iodine vapour. The author concludes that the conditions which tend to decrease the amount of vapour adsorbed by a powdered solid are the elevation of equilibrium temperature and the lowering of equilibrium pressure, both being reversible; further, the temperature and duration of heating to which the solid has been subjected beforehand produce an effect which is irreversible. Reasons are given for the inference that the preliminary heating results in diminution of the surface available for adsorption. H. J. E.

**Catalysis by Platinum Black.** G. VAVON and A. HUSSON (*Compt. rend.*, 1922, **175**, 277—279).—A platinum black catalyst which has become poisoned and inactive in the hydrogenation of a particular substance is not necessarily inactive towards another substance, and experiments were undertaken to determine the point at which absorption of hydrogen ceased with various unsaturated substances when the catalyst was progressively poisoned by the gradual addition of small quantities of carbon disulphide. This limiting point was found to vary with the nature of the substance, with the nature of the solvent, with the quality of the platinum, and with the amount of catalyst used, but is independent of the concentration of the solution. In one instance, using *5·5 grams of substance, 50 c.c. of alcohol, and 0·2 gram of platinum*, the amount of carbon disulphide required to inhibit hydrogenation was 1·1 mg. for *cyclo*hexene, 0·8 mg. for nitrobenzene, 0·5 mg. for cinnamic acid, and 0·4 mg. for acetophenone, so that a catalyst which was inactive towards acetophenone would still hydrogenate nitrobenzene or *cyclo*hexene. The author advances a physical explanation of the phenomenon, based on the adsorption of hydrogen by the metal. G. F. M.

**Rôle of Protective Colloids in Catalysis. II.** THOMAS IREDALE (T., 1922, **121**, 1536—1542).

**Catalytic Addition of Hydrogen. Influence of Oxygen on the Catalyst.** W. NORMANN (*Ber.*, 1922, **55**, [*B*], 2193—2197).—Working under conditions which are considered to exclude the presence of oxygen and with hydrogen which is free from any trace of the latter, the author has been able to effect the hardening of cotton-seed oil in the presence of nickel (prepared by the reduction of the chloride or cyanide), nickel powder, or palladised kieselguhr. It appears therefore that Willstätter's assumption of the necessity for the presence of oxygen is invalid. H. W.

**Ion Activities in Homogeneous Catalysis. Formation of *p*-Chloroacetanilide from *N*-Chloroacetanilide.** HERBERT S. HARNED and HARRY SELTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 1475—1484).—From theoretical considerations, it is deduced that in reactions in liquid systems catalysed by specific ions, it is the activities of such ions which determine the velocity of the reaction at any temperature when the catalysis depends on successive states of equilibria. The velocity constants of the conversion of *N*-chloroacetanilide into *p*-chloroacetanilide catalysed by hydrochloric acid have been determined at 17·65°, 25°, and 35° for concentrations of acid from 0·1*N* to 1·0*N*. This reaction according to Orton and Jones (*Brit. Assoc. Rep.*, 1910, 85) takes place thus :

$$(1)\ CH_3{\cdot}CO{\cdot}NCl{\cdot}C_6H_5 + H^{\cdot} + Cl' \rightleftharpoons CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + Cl_2;$$

$$(2)\ CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + Cl_2 \longrightarrow CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl + H^{\cdot} + Cl';$$

reaction (1) is measurably slow, whilst reaction (2) is very rapid, so that the system approximates to a continuous series of successive equilibria and fulfils the conditions stated above. It is shown that the velocity constants at each temperature are proportional

to the product of the activities of the hydrogen and chlorine i of the catalysing acid. The present work is the first case wh homogeneous catalysis has been calculated with exactitude ove wide range of concentration and in concentrated solutions, with uncertainties arising in liquid junction potentials. The te perature coefficient has been considered and the critical increm roughly calculated and shown to vary considerably with rise temperature. The relationship $K_T = k/\alpha_H \alpha_{Cl'}$, which holds exac for solutions of hydrochloric acid alone, fails when acid–s mixtures are used as catalysts. J. F. S

**A Possible Reconciliation of the Atomic Models of Bo and of Lewis and Langmuir.** W. HUGHES (*Nature*, 1922, 1 37—38).—If it is assumed that the electron shells are fixed a the nucleus rotates on an axis, a model is obtained which, wh viewed with respect to the electron shells, is precisely the sa as the Lewis-Langmuir model, with its very satisfactory rep sentation of the mechanism of chemical combination; when view with respect to the whole atom, it possesses all the merits of Boh model, yielding an accurate explanation of the reaction of ato and molecules with radiation. Further, the existence of isoto can be predicted with its aid, for if the nucleus of a given at possesses more than one stable axis of rotation with respect itself, or to its surrounding shells of electrons, or to both, a these axes are associated with different amounts of energy, it possible for the mass of the atom to be different for the differe positions of the nuclear axis, since by the theory of relativi energy possesses mass. A. A. E.

**Atomic Structure.** MAURICE L. HUGGINS (*Science*, 19 **55**, 459—460).—As an extension of Lewis's (A., 1916, ii, 31 theory of atomic structure, it is assumed that, although the numb of electrons in each shell of the lighter atoms is the same as in t original theory, the fifth, sixth, seventh, and eighth electrons the second and third shells pair with the first four, the distan between the electrons in each of these pairs, and also in each pa formed by bonding between atoms, being much less than the distan between pairs. The shells are therefore tetrahedra of pairs inste of cubes of single electrons. The electrons in each shell after t second tend to be placed opposite to the centres of the faces of t imaginary polyhedron formed by the electron groups in the unde lying shell. When the nuclear charge becomes sufficiently grea the same forces which cause pairing of electrons in nitrogen resu in the formation of triplets in the inner shells of the heavier aton As one after another of the outer electrons is drawn into an inn shell to form triplets, the remaining pairs are pushed further fro the nucleus, with possible rearrangement of the kernel structu The theory is applied in a number of instances. A. A. E.

**The Quantum Mechanism in the Atom.** E. T. WHITTAKI (*Proc. Roy. Soc. Edin.*, 1922, **42**, 129—142).—Ewing's model ferromagnetic induction (*Proc. Roy. Soc. Edin.*, 1922, **42**, 30) employed to investigate the mechanism within the atom whi

*compels all exchanges between kinetic energy and radiant energy* to conform with the equation $U=h\nu$. In this model, a system of magnets is rigidly connected like the spokes of a wheel, having poles of the same name at the circumference and poles of a coutrary sign at the centre of the circle. When an electron approaches *such a model in the direction of the axis of the wheel, a rotation* of the poles occurs which constitutes a magnetic current. The kinetic energy of the electron is expended in setting the magnetic structure of the atom in motion. When the velocity of the electron exceeds a critical value $2eM/\sqrt{Am}$, the magnetic structure is penetrated; $M$ and $A$ are quantities dependent on the atomic structure with which the electron collides. When its energy is less than this quantity, it is repelled without permanent loss of energy, the encounter being perfectly elastic. On penetrating the atom, the electron gives up $2e^2M^2/A$ of its energy and leaves the system with the remainder. This absorbed energy, which appears in the atom as a magnetic current, does not depend on the mass of the electron, but on its charge and on quantities dependent only on the atomic structure. This rotatioual energy is transformed into a radiant form by means of Hertzian oscillators. This view of the mechanism leads to the Planck equation $h\nu=U$. The emission of an electron already in the atom is a converse process and thus the equations may be applied to explain photo-electric phenomena. The connexion with the Bohr theory of series spectra is developed. W. E. G.

**The Quantum Mechanism in the Atom.** (SIR) J. ALFRED EWING (*Proc. Roy. Soc. Edin.*, 1922, **42**, 143—146).—A discussion of the mechanism suggested by Whittaker (see preceding abstract) for the conversion of the rotational energy of the wheel atom into radiation. There are two magnetic systems in his model of the atom: a central one forming the wheel, and another around it, which may be called the ring. An electron passing through the system produces relative angular displacement of the two parts of the atom, and magnetic forces are set up which tend to restore the whole to the original configuration. Thus oscillations are set up which expend their energy in the emitted radiation.

W. E. G.

**The Quantum Mechanism in the Atom.** R. A. HOUSTOUN (*Proc. Roy. Soc. Edin.*, 1922, **42**, 221—222).—The Whittaker model is checked numerieally. A calculation of the radius of the magnetic orbit gives values in satisfactory agreement with the dimensions of the hydrogeu molecule. It is shown that the Planck constant comes out as the product of the unit electric charge and a unit magnetie quantity. It thus has the correct dimensions.

W. E. G.

**The Importance of Whittaker's Atomic Model and of other Atomic Models.** W. PEDDIE (*Proc. Roy. Soc. Edin.*, 1922, **42**, 223—224).—A general discussion of the Whittaker model pointing out the inadequacy of the simply constituted atom of the electronic type. W. E. G.

**Sizes of Atoms in Diamond Type Crystals.** ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1922, **44**, 1497—1498).—On the basis of the results published in a recent paper (this vol., ii, 428), the author has recalculated the atomic radii of several elements of the rare gas type crystallising in the diamond type lattice. The following values are recorded: diamond 0·77 Å.U., silicon (S, Cl) 1·17 Å.U., germanium (Cu, Zn, Br) 1·22 Å.U., grey tin (Ag, I) 1·40 Å.U. The following interatomic distances are calculated: silicon carbide, 1·94 (1·90, 1·95); zinc sulphide, 2·39 (2·35, 2·35); cuprous chloride, 2·39 (2·38, 2·43); cuprous iodide, 2·62 (2·63, 2·78); silver iodide, 2·80 (2·83, 3·18); and cuprous bromide, 2·44 (2·52, 2·57). The values are given in Ångström units, and for comparison purposes the experimental value and the value from Bragg's atomic radii are included in brackets, the former value being placed first. J. F. S.

**The Properties of Elements and Salts as Related to the Dimensions of Atoms and Ions.** GEORGE L. CLARK (*Science*, 1922, **55**, 401—405).—It is shown that a considerable number of the properties of elements and salts are linearly related to the dimensions of the component atoms and ions. The relations are more general than those found by Biltz (A., 1921, ii, 487); thus it is found that if the atomic volumes of the five alkali elements are plotted on one axis (as the $X$-axis) of a three-dimensional rectangular co-ordinate system, the atomic volumes of the four halogens on the $Z$-axis, and the molecular volumes of the alkali haloids on the $Y$-axis, all the points (except some for cæsium, the anomaly of which is attributed to difference in crystal-lattice form) lie approximately on a plane $z=bx+cy+d$ which passes nearly through the origin. When other properties are plotted on the $Y$-axis, in a very large number of cases the surface, whilst not a plane, is of a simple form ("doubly ruled surface"). The surfaces may commonly be expressed by the equation $z=axy+bx+cy+d$. By using this method, a number of possible new linear relationships may be predicted. Values already ascribed to the atomic and ionic radii of the halogens and alkali elements are considered, Henglein's procedure being regarded as questionable. A. A. E.

**Atomic Radii. I.** MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 346—353).—Bragg's (A., 1920, ii, 537) "atomic spheres" and "atomic radii" may, when considered from the point of view of Lewis's theory of atomic and molecular structure (A., 1916, ii, 310), be given a definite physical meaning. The "atomic sphere" of an atom is its valency shell, and its "atomic radius" is the distance from the atomic centre to a group of electrons (usually an electron-pair) in the valency shell. It is shown that Bragg's assumption, that the distance between two adjacent atomic centres is equal to the sum of their radii, is often not valid, since in many cases the group of electrons constituting the bond does not lie on the line joining the atomic centres; that is to say, the two "atomic spheres" overlap. Eight causes of variation of the atomic radius

of an element are considered, namely: (1) some of the valency pairs may not act as bonds, (2) a valency electron-pair may be forced away from its normal position in the valency shell, (3) widely varying pulls are exerted on electron-pairs by atoms of different elements, (4) an atom of the same element in different structures may pull an electron-pair away a different distance from the nucleus of the atom to which it is linked, (5) if an atom has a different number of electron-pairs in its valency shell in two crystals, their distances from the nucleus would not be expected to be the same, (6) valency electron-pairs are pulled out from the nucleus to a different extent, according to whether they are on the centre-lines or not, (7) many atoms are capable of more than one arrangement of electrons in that part of the atom inside the valency shell, (8) the number of electrons constituting a bond may be more than two. A. A. E.

**Structure of the Ions of the Rare Earths.** H. G. GRIMM (*Z. physikal. Chem.*, 1922, **101**, 403—409).—A theoretical paper in which, on the basis of Bohr's arrangement of the electrons in xenon and niton, an attempt is made to draw conclusions on the structure of the ions of the rare earths, quinquevalent tantalum, sexavalent tungsten, and octavalent osmium ions which shall be in keeping with the chemical properties of these elements. It is shown that the outside sheath of the ions of the rare earths contains in all probability the same number of electrons, namely, eight or nine. The molecular volume and basicity series of the rare earths has been used to draw conclusions on the series of ionic radii (cf. A., 1921, ii, 127). J. F. S.

**Periodic System of the Atomic Ions.** H. G. GRIMM (*Z. physikal. Chem.*, 1922, **44**, 410—413).—The author has constructed a table on the basis of the structure of the ions of the elements. This divides the elements into six groups, namely, those with no electrons in the outer sheath, those with two electrons in the outer sheath, those with eight and eighteen electrons, respectively, in the outside sheath. The last three groups are composed of elements which are built up of completed sheaths, that is, sheaths occupied by the same number of electrons as in sheaths of the inactive gases. The fifth group contains elements with an incomplete outside sheath, and the sixth group contains elements with an incomplete inner sheath but a constant outside sheath. The elements of the sixth group are those of the rare earths. In the table the anions lie to the left of the inactive gases and the kations to the right. In this arrangement several elements, such as $Cl^-$, $Cl^{+++++++}$, $Se^{--}$, and $Se^{++++++}$, occur in two positions. J. F. S.

**Structure of some Gaseous Molecules of which Hydrogen is a Constituent.** A. O. RANKINE (*Trans. Faraday Soc.*, 1922, **17**, 719—727).—From viscosity measurements the following values have been deduced for the respective magnitudes (expressed in $cm.^2 \times 10^{-15}$) of the molecular "mean collision areas" of certain gaseous compounds containing hydrogen: HCl, 0·676; HBr,

0·763; HI, 0·926; $H_2S$, 0·773; $NH_3$, 0·640; $PH_3$, 0·911; AsH 0·985; $CH_4$, 0·772. The corresponding values for the inert gas have been recalculated and found to be as follows: Ne, 0·41 A, 0·648; Kr, 0·757; X, 0·915. Adopting the Lewis-Langmu view of the mechanism of combination between hydrogen aton and other elements, and assuming, on the basis of W. L. Bragg X-ray measurements (A., 1920, ii, 537), that the atoms towar the end of each period of the periodic table are equal in size, is shown to be probable that as the number of hydrogen aton in the molecule increases, their nuclei become more remote fro the nucleus of the central atom. This retreat of the hydroge nuclei is due to their mutual repulsion, and eventually leads t the failure of the formation of molecules, otherwise possible, suc as $BH_5$ and $AlH_5$. The relative dimensions of $CH_4$ and Kr agr to within the limit of probable experimental error. It is to b anticipated, therefore, that $NH_4$ and Rb, which are correspondingl related to $CH_4$ and Kr, respectively, would occupy nearly equ spaces. This is confirmed from crystallographic data.

J. S. G. T.

**Arabic Chemistry.** E. J. HOLMYARD (*Nature*, 1922, **10**, 778—779).—An historical note ascribing to Maslima al-Majrī the authorship of the section on chemistry in the "Letters" o the Brethren of Purity (10th century A.D.). A. A. E.

**[Lecture Experiment.] Time Reaction.** MARTIN MEYE (*J. Amer. Chem. Soc.*, 1922, **44**, 1498—1500).—A time reactio of the same type as that recently described by Forbes, Estill, an Walker (this vol., ii, 271) which is suitable for a lecture exper ment is described. For example, 40 c.c. of *M*-sodium thiosulphat 20 c.c. of 1·67*M*-potassium hydroxide containing 0·67*M* of potassiu sodium tartrate and 44·46 grams of antimony trioxide per litre, a mixed and 10—15 c.c. of 4*N*-hydrochloric acid added. After a induction period of thirty to sixty seconds, a white turbidity appea which changes to the characteristic orange colour of antimon trisulphide. Variations of the quantities give different inductio periods. J. F. S.

## Inorganic Chemistry.

**New Revision of the Density of Oxygen Gas.** E. MOLE and M. CRESPI (*Anal. Fís. Quím.*, 1922, **20**, 190—192; cf. Mol and González, this vol., ii, 497).—Oxygen prepared from potassiu permanganate contains traces of carbon dioxide and ozone ar purification by phosphoric oxide is insufficient. Determinatio on oxygen from potassium permanganate from which carbon dioxi and ozone had been removed by soda-lime and mercury, respectivel

gave the value (calculated for lat. 45°) 1·42895 for the density of the gas. This is in good agreement with the value previously given (*loc. cit.*). G. W. R.

**Ozone.** E. H. RIESENFELD and G. M. SCHWAB (*Ber.*, 1922, **55**, [*B*], 2088—2099).—The main difficulty in the preparation of pure ozone and the determination of its physical constants consists in its explosiveness. The recent advances in micro-analytical methods have enabled the authors to perform the necessary experiments with such small quantities of material that explosions are avoided or are not dangerous.

Dry oxygen is ozonised in the usual manner and the product condensed in small glass bulbs with long capillaries immersed in liquid air (the apparatus is figured and fully described in the original communication). Since the condensate is always richer in ozone than the supernatant gas, the latter is pumped away after each condensation and the vessel again filled with ozonised oxygen. When in this manner a dark blue condensate (solution of oxygen in ozone) has been obtained, the subsequent condensates consist of pale blue solutions of ozone in oxygen; when the exhaustion is renewed, the oxygen evaporates and the ozone passes into the first phase. The dark blue product still contains about 30% of oxygen, but its removal can be fairly readily effected by fractionation, since the boiling points of oxygen and ozone differ by about 70°. At the temperature of liquid air, the vapour pressure of liquid ozone is practically negligible so that the glass bulbs can be evacuated completely and the capillaries sealed off without danger. Analysis of the product is effected by breaking one of the bulbs containing a known weight of substance under potassium iodide solution containing boric acid, measurement of the volume of inactive oxygen, and estimation of that of active oxygen by titration with sodium thiosulphate. Within the limits of experimental error, the volume relationship of active to inactive oxygen is 1 : 2 and the purity of the ozone is controlled further by a micro-estimation of the molecular weight by Dumas's method. The following physical constants have been determined (the methods and requisite apparatus are fully described and figured in the original); m. p. −250°, b. p. −112·3°, critical temperature −5°, $d^{-183}$ 1·784. Liquid ozone is not completely miscible with liquid oxygen at all temperatures, the critical temperature of solubility lying at −158°.

Very discordant results have been obtained during investigations of the thermal production of ozone from oxygen. According to the Nernst theorem, a minimal temperature of 4000° Abs. is necessary for the production of appreciable quantities of ozone, whereas Fischer has observed considerable formation of the gas at glowing Nernst filaments at a much lower temperature. The temperature attained in the explosion of pure ozone is calculated to be about 4000° Abs., and under these conditions a distinct odour of ozone is observed. On the other hand, no trace of ozone could be perceived in explosions of mixtures of ozone and oxygen

*with which a temperature of more than 2000° Abs.* was obtained A purely thermal production of ozone is not involved, therefore in Fischer's experiments.

The explosive decomposition of ozone is very sensitive tc *catalytic influences, but if these are excluded the gas is found tc* be unexpectedly stable. According to Warburg's calculation, th( half life period of pure ozone at 16° is one hundred and sixty seven hours, whereas the authors find that under certain con ditions a period of several weeks elapses before decomposition ha proceeded to this extent.

Violent changes of pressure cause the explosion of ozone in al states of aggregation. An explosion when the solid or liqui( material is lightly touched or on sudden solidification of the liqui( has not been observed.

The authors consider that their work brings conclusive evidenc( against the existence of oxozone. H. W.

**The Oxidising and Reducing Properties of Sulphu Dioxide. I. Mercury Chlorides.** LACHLAN MACQUARI STEWART and WILLIAM WARDLAW (T., 1922, **121**, 1481—1489).

**The Physical Properties of Sulphur Trioxide.** A BERTHOUD (*Helv. Chim. Acta*, 1922, **5**, 513—532).—Doubt i thrown by the author on the existence of sulphur trioxide i the so-called α- and β-forms. The fact that the two kinds ca exist together indefinitely, with other observations of a simila *character, indicates that the silky crystals, the so-called β-form* are a product of hydration. The compound, if compound it be must be, however, of a unique type, containing something like thousand or more mols. of sulphur trioxide to one of water. *number of physical properties of sulphur trioxide were determine* with the greatest care. It has m. p. 16·85°±0·02, agreeing closel with Lichty's result, 16·79° (A., 1912, ii, 1164) and b. p. 44·52°/76 mm. The vapour pressure curve, as deduced from determination at 15 points between 24° and 47·8°, is represented by $\log p = -2314/T + 10{\cdot}17$. The critical pressure and temperature wer determined, using a modification of Pellaton's method (cf. A. 1916, ii, 245), and the critical temperature by direct observatio of the disappearance and reappearance of the meniscus. Th results are, $p_c$=83·8 atm., $t_c$=218·3°. The density was determine at temperatures from 17° to 55° by a pycnometer method, and fro 98° to 214° by a modification of Young's method (T., 1891, **59**, 37) which gives the density of both liquid and vapour. The critica density, $d_c$, is 0·633. The surface tension was determined by th method of Ramsay and Shields, the results being, at 19°, 44·9 and 78·0°, respectively, γ=34·17, 29·47, and 22·63. The molecula heat of vaporisation, calculated from the vapour tension curve *is 10,300 cal.* The *quotient L/T,* Trouton's *ratio, is surprisingl* high, 32·5, the normal for liquids of similar b. p. being 21·0; th high value indicates association in the liquid form. The valu of Eötvös's surface tension coefficient also indicates associatio of the liquid at lower temperatures, but at 78° the value is nearl

*normal.* The values of van der Waals's *constants are* : $a=0{\cdot}01629$; $b=0{\cdot}002684$. E. H. R.

**Preparation of Selenium Dioxide.** JULIUS MEYER (*Ber.*, 1922, **55**, [*B*], 2082—2084).—Selenium in quantities of 60—75 grams is heated to its melting point in a porcelain boat placed in a wide hard glass tube; a very rapid current of oxygen which has been passed through fuming nitric acid is passed over it, causing the molten selenium to burn with a brilliant blue flame and to give a sublimate of selenium dioxide the purity of which increases with increasing rate of the supply of oxygen. The product, which contains small quantities of oxides of nitrogen, is purified by being sublimed in the same tube in a current of pure oxygen. To avoid loss of material, the tube is connected with a doubly tubulated vessel of two *litres* capacity in which the final traces of the dioxide are deposited. The combustion of 60—70 grams of selenium can be effected in about one and a quarter hours.

The *oxidation of selenium appears to be greatly affected by catalytic influence, acidic substances causing acceleration whereas* alkaline *materials* (*including glass*) cause *retardation.* H. W.

**Active Hydrogen and Nitrogen.** GERALD L. WENDT (*Nature*, 1922, **109**, 749).—Newman's (this vol., ii, 279) failure to obtain a test for nitrides when sulphur, phosphorus, and iodine are treated with active nitrogen is not evidence of the absence of chemical reaction; in the cases of sulphur and phosphorus, the formation of sulphides and phosphides has been demonstrated by the author, whose experiments also show that phosphine and hydrogen sulphide are formed when phosphorus and sulphur are exposed to active hydrogen. A. A. E.

**Active Hydrogen and Nitrogen.** F. H. NEWMAN (*Nature*, 1922, **109**, 749; cf. Wendt, preceding abstract).—The absorption of active nitrogen by sulphur, phosphorus, and iodine probably results in chemical combination, since the absorbed gas is not liberated on heating; in the case of active hydrogen, however, absorption occurs at temperatures above 0°. This absorption may be due in part to chemical action, but other processes, such as occlusion, have to be taken into account. A. A. E.

**Reaction between Cathodic Hydrogen and Nitrogen at High Pressures.** J. N. PRING and E. O. RANSOME (*Trans. Faraday Soc.*, 1922, **17**, 689—694).—When hydrogen is liberated electrolytically at a cathode in contact with nitrogen, particularly at high pressures, the conditions would appear to be favourable to the synthesis of ammonia. A solution of sulphuric acid was electrolysed in the presence of nitrogen at pressures ranging from 1 to 500 atmospheres. At atmospheric pressure, the mean percentage yield of ammonia by direct union of the elements was 0·04%. At pressures from 60 to 104 atmospheres, the yield of ammonia was 0·09%. For pressures ranging from 300 to 500 atmospheres, no ammonia was synthesised. The results indicate

that no reaction occurs between nitrogen and cathodic hydrogen, the small yield of ammonia at the lower pressures being due to thermal action. J. S. G. T.

**Hydroxylamine.** CARL KJELLIN (*Svensk Kem. Tidskr.*, 1921, **33**, 213—228).—In the reaction expressed by the equation: $NH_2{\cdot}OH+2Fe(OH)_2+H_2O=NH_3+2Fe(OH)_3$, the experimental results are in practically complete accord when the potassium hydroxide in the solutions does not exceed 1·75%. The reactions between hydroxylamine and stannous hydroxide and manganese hydroxide were also examined; the former yields ammonia in moderate agreement with theory, whilst in the latter case the amount of ammonia produced is negligible. The change undergone when hydroxylamine is subjected to heat in presence of aqueous potassium hydroxide appears to be expressed by the equation: $3NH_2{\cdot}OH=3H_2O+NH_3+N_2$. Compounds of the type $CH_2R{\cdot}NH{\cdot}OH$ (R=Me, Et, Pr) when hydrolysed in concentrated hydrochloric acid or potassium hydroxide, evolved up to 75% of the expected yield of ammonia. It is probable that *N*-*iso*propylhydroxylamine and bromine react in accordance with the scheme: $CHMe_2{\cdot}NH{\cdot}OH \longrightarrow CHMe_2{\cdot}NBr{\cdot}OH \longrightarrow CHMe_2{\cdot}NO \longrightarrow CMe_2{:}NOH$. *N*-Ethylhydroxylamine hydrochloride forms long, colourless, hygroscopic crystals, m. p. 37°.

CHEMICAL ABSTRACTS.

**Crystal Structure of Phosphonium Iodide.** ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1489—1497).—The structure of the crystals of tetragonal phosphonium iodide has been investigated by means of *X*-rays, using chiefly Laue photographs. It is shown that the *X*-ray data are satisfactorily accounted for by a structure obtained by placing in a unit cell of the dimensions 6·34×6·34×4·62 Å.U. phosphorus atoms at (000) and ($\frac{1}{2}\frac{1}{2}0$) and iodine atoms at ($0\frac{1}{2}u$) and ($\frac{1}{2}0\bar{u}$) where u has a value very close to 0·40, and it is shown that no simpler structure is capable of accounting for the data. The close relationship between this structure and the low temperature form of ammonium chloride is demonstrated. J. F. S.

**Hypophosphorous Acid. IV. Its Reaction with Cupric Chloride.** ALEC DUNCAN MITCHELL (T., 1922, **121**, 1624—1638).

**The Volatilisation of Arsenic and Antimony by means of Methyl Alcohol.** L. DUPARC and L. RAMADIER (*Helv. Chim. Acta*, 1922, **5**, 552—556).—By passing a current of air through a solution of arsenious or antimonious oxide in concentrated hydrochloric acid containing a suitable proportion of methyl alcohol, the whole of the arsenic or antimony can be carried over into an absorbing solution. In this way, 0·1 gram of arsenious oxide can be volatilised in one hour at 55° in 45 c.c. of methyl alcohol. In the case of antimonious oxide the vaporisation can be completely prevented by diluting the hydrochloric acid used with an equal volume of water. The method may be applicable for

eparating arsenic and antimony from other metals and from each ther. E. H. R.

**Revision of the Atomic Weight of Boron. Analysis of Boron Trichloride.** O. HÖNIGSCHMID and L. BIRCKENBACH Anal. Fis. Quim., 1922, **20**, 167—173; cf. A., 1921, ii, 646).—rom determinations of the ratio $BCl_3 : 3Ag$ and $BCl_3 : 3AgCl$, ollowing the methods used in the authors' revision of the atomic eight of bismuth (*loc. cit.*), the values of the atomic weight of oron obtained for three samples of specially purified boron trihloride were 10·840, 10·818, and 10·825, respectively. The first alue is rejected and the value 10·82 is taken. It is pointed out 1at this value is in better accord with the theory of isotopes than 1e hitherto accepted value of 10·90. G. W. R.

**The Action of Diamond n Carbon Monoxide.** FOIX (*Bull. oc. chim.*, 1922, [iv], **33**, 678—679).—*An attempt to carry out he reaction* $CO_2 + C \rightleftharpoons 2CO$ *in the case of the diamond at temeratures above 1100° resulted in the deposition of amorphous arbon on the surface of diamond without the latter undergoing ny change. The conclusion is drawn that the time of experiment, ree hours, was insufficient for the attainment of equilibrium.*
H. J. E.

**The Preparation of Carbon Suboxide on a Larger Scale nd the Properties of Pure Carbon Suboxide.** ERWIN OTT nd KARL SCHMIDT (*Ber.*, 1922, **55**, [*B*], 2126—2130).—Diacetylartaric anhydride is heated to its boiling point in a flask the neck f which is connected to a cylinder in which an electrically heated latinum wire is suspended. The upper portion of the cylinder connected through a series of condensing vessels to a powerful ump which, in spite of the evolution of carbon monoxide, mainains a pressure of about 11 mm. (The apparatus is fully figured nd described in the original.) The decomposition of one hundred nd eighty-nine grams of anhydride can be effected in six to eight ours, the yield of carbon suboxide being 41% of that theoretically ossible. From this point of view the process is superior to the nproved method of Stock and Stoltzenberg (A., 1917, ii, 308), hich depends on the action of phosphoric oxide on malonic acid, nd has the further advantage of greater cheapness. In addition, 1e carbon suboxide obtained in this manner can be preserved nchanged (except for a slight darkening of colour which is probbly due to incompleteness in the exclusion of moisture) for long eriods, whereas that prepared with the help of phosphoric oxide ipidly becomes polymerised, probably owing to the presence of aces of phosphorous oxide in the latter (cf. Manley, T., 1922, **121**, 31). H. W.

**The Crystal Structure of Quartz.** MAURICE L. HUGGINS *Physical Rev.*, 1922, **19**, 363—368).—The suggested structure of uartz, obtained by means of the Lewis theory, is in accord with ragg's conclusions. Each silicon atom is surrounded by four airs of electrons at tetrahedron corners, which act as bonds

*connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electron-pairs, two of which serve as bonds connecting the oxygen to silicon* atoms. The crystal is thus not composed of silica units, but is a single molecule. A. A. E.

**Solubility of Helium in Water.** HAMILTON P. CADY, HOWARD M. ELSEY, and EMILY V. BERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1456—1461).—The solubility of helium has been determined at a series of temperatures lying between 2° and 30°, using material which was spectroscopically pure. The following values of the absorption coefficient are recorded: 2°, 0·00938, 10°, 0·00895, 25°, 0·00861, and 30°, 0·00817. Plotting these values shows that there is no indication of the solubility passing through a minimum as has been repeatedly stated. The values are all smaller than those of Estreicher (A., 1900, ii, 205) and Antropoff (A., 1919, ii, 511), and larger than the single determination of Ramsay (T., 1895, **67**, 697). J. F. S.

**The Preparation of Sodium Hydrogen Carbonate.** ER. TOPORESCU (*Compt. rend.*, 1922, **175**, 268—270).—A study similar to that originally made at 15° (this vol., ii, 375) of the equilibrium of the four salts, sodium chloride, sodium hydrogen carbonate, ammonium chloride, and ammonium hydrogen carbonate with their saturated solutions has now been made at 35° and 50°. The geometric representation of the results obtained by means of a Le Chatelier diagram enables a calculation to be made of the theoretical yield, that is to say, the proportion of sodium chloride transformable into crystalline sodium hydrogen carbonate for a solution of any given initial composition. G. F. M.

**The Preparation of Ammonium Chloride at Low Temperatures.** PAUL MONDAIN-MONVAL (*Compt. rend.*, 1922, **175**, 162—164).—The conditions governing the crystallisation of ammonium chloride at 0° from solutions containing in addition one or more of the salts sodium chloride, sodium carbonate, and ammonium carbonate, were studied in a similar manner to those previously described for 15°, and a Le Chatelier diagram is given showing the surfaces of saturation. The zone of crystallisation of sodium carbonate shows two distinct areas, one corresponding with the crystallisation of $Na_2CO_3,10H_2O$, and the other with a hydrate of the formula $2Na_2CO_3,5H_2O$, the existence of which, although disputed by Wegscheider (A., 1912, ii, 156), is now confirmed. G. F. M.

**A Preliminary Attempt to Transmute Lithium.** RALPH W. G. WYCKOFF (*Science*, 1922, **55**, 130—131).—Inconclusive results were obtained when lithium or its salts was bombarded with a stream of electrons, in the hope of introducing one or two electrons into the nucleus, and detecting spectroscopically the formation of helium or hydrogen. A. A. E.

**Electrolytic Preparation of Calcium Amalgam.** B. S. NEUHAUSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1445—1447).—The author discusses the methods which have been adopted previously for the preparation of calcium amalgam (Smith and Bennett, A., 1909, ii, 663; 1910, ii, 500), and devises a more efficient method of preparing this material. The method consists in just covering the bottom of a crystallising dish, 25 cm. diam., with a layer of mercury which serves as cathode, and then filling the dish with a 1·75*N*-solution of calcium chloride. An anode of platinum foil (2×4 cm.) is placed in the solution parallel to the mercury surface at a distance of 4 cm., and a current of 3·5 amperes at 4·6 volts passed for thirty minutes. This arrangement prevents heating and foaming. After about thirty minutes, the generation of hydrogen sets in, but up to this point the solution remains neutral to litmus and there is no formation of a black powder which in other methods always forms and catalyses the decomposition of the amalgam. The amalgam is washed by allowing it to fall in a fine stream into two litres of distilled water. The product prepared in this way contains 0·069—0·075% of calcium, and is preserved in a bottle filled with carbon dioxide. J. F. S.

**The Crystal Structures of Aragonite ($CaCO_3$) and Related Minerals.** MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 354—362).—A proposed structure for aragonite is such that, as in calcite, each carbon atom is linked by double bonds to three oxygen atoms, each oxygen atom to two calcium atoms and one carbon atom, and each calcium atom to six oxygen atoms, at the corners of an irregular octahedron. The observed cleavage of aragonite is in accord with the principles that (*a*) cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral, (*b*) where some bonds are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones, (*c*) all bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area. The structure of aragonite, and those of the isomorphous minerals strontianite, witherite, and cerussite, conform to the author's theory that the electron groups in an atomic shell tend to place themselves opposite to the faces of the imaginary polyhedron formed by the electron groups in the next underlying shell. A. A. E.

**Dispersoid Chemistry of Gypsum. II.** H. NEUGEBAUER (*Kolloid Z.*, 1922, **31**, 40—45).—The viscosity of suspensions of anhydrite, gypsum, burnt gypsum, dehydrated gypsum, anhydrasite, and leucolith has been measured at various intervals of time after preparation, with the object of investigating the mechanism of the hydration of calcium sulphate. It is shown that in opposition to the statements of van't Hoff the preparations used in the present work could not be completely dehydrated at 115° or slightly higher. The water of crystallisation was never reduced to less than 4%. The common dihydrate lost its crystal water at 102° considerably more slowly and less completely than the other forms,

probably because of the size of the crystals. The viscosimetric investigation of the commercial "van't Hoff gypsum" gave very indefinite curves, whereas van't Hoff found extremely rapid combination with water and rapid hardening for this material. The formation of soluble anhydrite does not come into the question here. Gypsum prepared by slowly dehydrating precipitated calcium sulphate gave a normal combination curve, and the dihydrate gave curves analogous to those obtained with insufficiently dehydrated gypsum. A commercial product, anhydrasite, prepared by the dehydration of natural anhydrite, exhibits, on dehydration, a behaviour analogous to that shown by "van't Hoff gypsum." Its viscosity curve is more pronounced than that of commercial gypsum obtained in the usual way, but less steep than that of precipitated gypsum. Towards the addition of alum it behaves in the same way as plaster of Paris. A further technical product, leucolith, showed no combination with water from its viscosity measurements. The behaviour in this case was analogous to that of estrich gypsum (flooring cement), the setting in these cases being due to the presence of free lime. J. F. S.

**The Constitution of Strontium-Lead Alloys.** E. Piwowarsky (*Z. Metallk.*, 1922, **14**, 300—301).—Lead and strontium form one compound, $Pb_3Sr$, melting at 676° and containing 12·35% Sr, and a eutectic, containing very small amounts of strontium, which melts at the same temperature as lead. Strontium is completely insoluble in solid lead. [Cf. *J. Soc. Chem. Ind.*, 1922, Sept.] A. R. P.

**Barium Sulphuric Acid and Barium Selenic Acid.** Julius Meyer and Walter Friedrich (*Z. physikal. Chem.*, 1922, **101**, 498—503).—The solubility of barium sulphate in 97·86% sulphuric acid has been determined at 25° and found to be 14·91 grams in 100 c.c. of acid. The saturated solution is shown to contain barium sulphuric acid, $H_2[Ba(SO_4)_2]$, and by electrolytic transport this compound can be accumulated in the anode compartment, where it crystallises. Dissolving barium selenate in selenic acid gives rise to a similar compound, barium selenic acid, $H_2[Ba(SeO_4)_2]$, which can similarly be crystallised by electrolytic transport. A concentrated solution of selenic acid saturated with barium selenate also deposits crystals of barium selenic acid. J. F. S.

**Physical Chemistry of the Oxides of Lead. IV. Red Lead and Lead Sesquioxide.** Samuel Glasstone (T., 1922, **121**, 1456—1469).

**Physical Chemistry of the Oxides of Lead. V. The Electromotive Behaviour of Lead Dioxide.** Samuel Glasstone (T., 1922, **121**, 1469—1480).

**Behaviour of Sulphides of Heavy Metals in Aqueous Solutions.** O. Weigel (*Sitzungsber. Ges. Naturw.* Marburg, 1921, No. 2, 35—50; from *Chem. Zentr.*, 1922, i, 182—183; cf. A., 1907, ii, 237).—The known solubilities of heavy metal sulphides

as experimentally determined are generally greatly in excess o the values calculated from their solubility products. The author' determinations of the solubilities of the sulphides of thallium silver, and lead show that in each case the calculated solubility i less than that determined experimentally. From the effect c lead ions on the solubility of lead sulphide and the potential of lead sulphide electrode, it is concluded that dissociation in aqueou solution takes place in successive stages and that most of th dissolved substance is in the form of complex ions. Removal c metallic ions by addition of sulphide ions depends on the formatio of complex ions. G. W. R.

**The Blue Flame produced by Common Salt on a Coal Fire** ARTHUR SMITHELLS (*Nature*, 1922, **109**, 745; cf. Merton, *ibid* 1922, **109**, 683).—A brief historical note on the recognition of th blue flame produced by common salt on a coal fire as being du to compounds of copper derived from pyrites in the coal.

A. A. E.

**The Rate of Combination of Copper and Phosphorus a Various Temperatures.** C. A. EDWARDS and A. J. MURPH' (*J. Inst. Metals*, Adv. Copy).—Penetration of copper rods b phosphorus vapour takes place at 640° at atmospheric pressur The dissociation-temperature curve for alloys of copper an phosphorus containing up to 30·8% of the latter indicates tl existence of the phosphides CuP and $Cu_5P_2$.

CHEMICAL ABSTRACTS.

**Corrosion of Copper by Salt Solutions.** W. MÜLLER (Z *Metallk.*, 1922, **14**, 286—295).—Copper is rapidly corroded by se water, sodium chloride, and magnesium chloride, with the formatio of a green, basic chloride which readily detaches itself from th metal and therefore does not form a protective coating. Wea solutions of magnesium and calcium sulphates corrode copper ve slowly, the metal becoming gradually covered with a white pr cipitate containing bluish-green flakes of basic sulphate. [C *J. Soc. Chem. Ind.*, 1922, Sept.] A. R. P.

**Critical Constants of Mercury.** S. WEBER (*K. Dansk Videnskab. Selskab. Math.-fys. Medd.*, 1920, **3**, No. 4; cf. A., 192 ii, 699).—The critical pressure of mercury is 1036 atmosphere If curves be plotted giving the density of liquid and vapour phas of mercury and hydrogen, the temperature and density bein written in terms of the critical temperature and density, the tw curves practically coincide. Vapour-pressure curves plotted in similar manner also coincide, hence it is concluded that hydroge at this low temperature is monatomic. CHEMICAL ABSTRACTS.

**Atomic Weight of Mercury from Different Sources.** J. N BRÖNSTED and G. HEVESY (*Nature*, 1922, **109**, 780; cf. this vol ii, 149).—Measurements of the density of mercury prepared b the same method from minerals of different origin exhibit n differences exceeding the possible experimental error, which corr

sponds with 0·0004—0·0012 in the atomic weight. It is therefore concluded, with great probability, that the isotopic composition of *mercury of terrestrial origin is the same.* A. A. E.

**Catalytic Decomposition of certain Oxides.** GUY B. TAYLOR and G. A. HULETT (*J. Amer. Chem. Soc.*, 1922, **44**, 1443—1445).—A theoretical paper in which the authors criticise the conclusions of Kendall and Fuchs (this vol., ii, 147). It is pointed out that in the system $HgO : Hg : O_2$ it is inadmissible to speak of the equilibrium pressure of oxygen at a fixed temperature without specifying the partial pressure of mercury. Further, the grounds on which Kendall and Fuchs maintain that their results are in agreement with those of Lewis (A., 1906, ii, 284) in connexion with the dissociation of silver oxide are considered to require explanation. The conclusions with regard to the decomposition of barium dioxide are also criticised, and it is pointed out that the explanation of the discrepancy between the authors' results (A., 1913, ii, 932) and those of Kendall and Fuchs does not meet the case.

J. F. S.

**Catalytic Decomposition of certain Oxides.** JAMES KENDALL and FRANCIS J. FUCHS (*J. Amer. Chem. Soc.*, 1922, **44**, 1447—1448).—An answer to the criticisms of Taylor and Hulett (cf. preceding abstract). J. F. S.

**Preparation of Pure Ceria-earth Compounds.** R. H. MANSKE (*Can. Chem. Met.*, 1922, **6**, 83—84).—A study of the solubility curves shows that if a saturated solution of the sulphates of *cerium (about 50%), lanthanum, praseodymium, and neodymium* at 0° is rapidly heated to 41°, the sulphates of lanthanum and neodymium crystallise with cerium sulphate, but free from praseodymium. Separation from cerium is easy. If the saturated solution of the sulphates were heated to 65°, lanthanum would crystallise free from praseodymium and neodymium so long as cerium was present. CHEMICAL ABSTRACTS.

**The Solubility of Gases in Aluminium.** J. CZOCHRALSKI (*Z. Metallk.*, 1922, **14**, 277—285).—Molten aluminium absorbs very little of the common gases below 900°, but with increasing temperature above this the amount absorbed and retained in the solid metal at ordinary temperatures increases approximately in the following order: nitrogen, carbon monoxide, air, oxygen, sulphur dioxide, carbon dioxide, illuminating gas, and hydrogen. In general, the gas is retained in the solid metal in numerous microscopic *blow-holes, but very small amounts of nitrides, oxides,* carbides, and sulphides are formed in atmospheres containing nitrogen, oxygen, carbon, or sulphur compounds. The technical significance of these facts is discussed with reference to the production and working of aluminium. [Cf. *J. Soc. Chem. Ind.*, 1922, Sept.] A. R. P.

**Mordants. II. Alumina.** WILDER D. BANCROFT (*J. Physical Chem.*, 1922, **26**, 501—536).—A general discussion on the

hydrolysis of aluminium salts and the adsorption of aluminium sulphate and alumina by wool, silk, and cotton. It is shown that all aluminium salts are hydrolysed to some extent in aqueous solution, and the amount of hydrolysis increases with increasing temperature. The actual hydrolysis is greater with salts of weak acids, but the apparent hydrolysis may be abnormally large in sulphate solutions owing to the coagulating effect of the sulphate ions on the colloidal alumina. Different fibres adsorb alumina to different degrees, wool having a much greater adsorbing power than cotton, and silk being probably slightly inferior to wool. Owing to this difference in specific adsorption, wool decomposes aluminium salt solutions which are distinctly acid, whilst cotton is effective only in more basic solutions. The colloidal alumina is taken up and held firmly. Coagulated alumina may be adsorbed to some extent, but it easily rubs off the material. It is probable that in all cases alumina is adsorbed and not a basic salt. The phenomena may be complicated by the fact that the alumina itself will adsorb some sulphuric acid, for example, and that the wool may, and probably does, adsorb some sulphuric acid also. Since alumina is adsorbed less strongly by cotton than by wool, it is also held less strongly by cotton than by wool. If to cotton is added some substance, such as tannin, which adsorbs alumina strongly, the cotton mordanted with tannin will be able to take alumina out of solutions of aluminium salts which are not decomposed by cotton alone, and alumina is held more strongly by mordanted cotton than by cotton alone. The increase in adsorbing power shown by mercerised cotton is due to structural differences in the cotton fibre. There is no evidence of the formation of any definite compound between alumina and either wool, silk, or cotton. J. F. S.

**Preparation of Metals by Goldschmidt's Aluminothermic Method. I.** Tôtarô Fujibayashi (*J. Chem. Ind. Japan*, 1922, **25**, 499—511).—Pure manganese and chromium free from carbon have been prepared by Goldschmidt's method. For the former, an intimate mixture of trimanganic tetroxide (100 parts), manganese dioxide or sesquioxide (15—20 parts), and 90% of the calculated weight of powdered aluminium was used, the yield being 85—90% of the theoretical value. The product contained 95—97% of manganese, the remainder being mainly aluminium. For the preparation of chromium, an intimate mixture of chromium sesquioxide (100 parts), calcium chromate (10—15 parts), and 90% of the calculated weight of powdered aluminium was used, the yield being 85—92% of the theoretical; the product contained 95—97% of chromium and 3—5% of aluminium. K. K.

**Reducing Action of Ferrous Hydroxide.** Susumu Miyamoto (*J. Chem. Soc. Japan*, 1922, **43**, 397—438).—Nitrites or nitrates can be estimated as ammonia by reduction with ferrous hydroxide in alkaline solution. In the case of the nitrite, the sample (0·1—0·3 gram) is boiled with 15 grams of ferrous sulphate and 200 c.c. of saturated alkali hydroxide solution and the evolved

ammonia is passed into sulphuric acid of known concentration as in Kjeldahl's method. Nitrates are not so easily reduced as nitrites, a reflux condenser must be attached to the boiling-flask instead of a bulb, and the boiling continued for three to three and a half hours, a current of hydrogen, nitrogen, or air being introduced into the flask to carry over ammonia. Ferrous hydroxide also reduces nitrobenzene to aniline at the ordinary temperature.

The velocity of reaction between potassium nitrite and ferrous hydroxide in alkaline solution was measured at 25°, 35°, and 45°. When the initial concentration of the nitrite is very small compared with that of the alkali hydroxide, the reaction is linear. The velocity constant increases with the concentration of the alkali hydroxide, and is expressed by the formula: $k=e^{A-B/P}(1+0{\cdot}79\,C_{KOH})$, where $A=20{\cdot}609$ and $B=8098{\cdot}2$. The velocity constant is increased 2·35 times for each elevation of 10° in temperature. The presence of potassium sulphate in the system has no effect on the reaction velocity. Attempts to measure the velocity at the boiling point, 108°, were unsuccessful, the reaction occurring too quickly.

The velocity of reaction between potassium nitrate and ferrous hydroxide in alkaline solution was measured at 108° and 112·2°, the velocity constant being approximately $7{\cdot}577\times10^{-3}$ (calc. $7{\cdot}726\times10^{-3}$; $C_{KOH}$: 5·5394 mol. per litre) and $2{\cdot}331\times10^{-2}$ (calc. $2{\cdot}326\times10^{-2}$; $C_{KOH}$: 6·9541 mol. per litre respectively).

The electric potentials of the following cells were measured at 25°, using $1N$-, $2N$-, $3N$-, $4N$-, and $5N$-sodium hydroxide solutions:

I. Pt. platinised|$NaOH,Fe(OH)_2,Fe_3O_4,xH_2O$|NaOH|HgO,NaOH|Hg; II. Pt. platinised $H_2$|NaOH|HgO,NaOH|Hg. III. Pt. platinised|$NaOH,Fe(OH)_2,Fe_3O_4,xH_2O$|NaOH|NaOH|$H_2$, Pt. platinised. The potential of I is expressed by $E_1=0{\cdot}8030-0{\cdot}0015\,C_{NaOH^2}$, that of II by $E_2=-0{\cdot}9270-0{\cdot}00332\log C_{NaOH}$, that of III by $E_3=0{\cdot}1240+0{\cdot}00332\log C_{NaOH}-0{\cdot}0015\,C_{NaOH^2}$. K. K.

**A New Iron Salt.** OTTO RÖHM (*Collegium*, 1921, No. **614**, 282—284).—When a concentrated solution of ferrous sulphate is oxidised with chlorine and the excess of water allowed to evaporate, a crystalline *substance* having the composition $FeSO_4Cl,6H_2O$ is obtained. This compound, which is neither a mixture nor a double salt, and does not deliquesce in damp air, may also be prepared (*a*) by heating 1 mol. of ferric chloride, 1 mol. of ferric sulphate, and 18 mols. of water, and (*b*) by heating 1 mol. of ferric chloride, 1 mol. of sulphuric acid, and 6 mols. of water, and driving off the hydrogen chloride formed. CHEMICAL ABSTRACTS.

**I. The Structure of Electrolytically Deposited Nickel. II. The Influence of Superposed Alternating Current on the Deposition and Solution Potential of Nickel.** V. KOHLSCHÜTTER and H. SCHÖDL (*Helv. Chim. Acta*, 1922, **5**, 490—512, 593—609).—I. Continuing the work of Kohlschütter and Vuilleumier (A., 1919, ii, 9) and Stäger (A., 1920, ii, 728) on the properties of electrolytically deposited nickel, experiments have been made with the object of determining whether there is any relation between

the micro-structure of the deposits and the contraction phenomenon which has been found to depend on the deposition potential. Comparative experiments were made, using direct current and alternatively direct current with a superposed alternating current, which considerably diminishes the observed contraction of the deposit. The previous conclusion was confirmed that, when deposits showing a high contraction are formed, deposition takes place at first in a thin deposit or skin of hydrogen. The same effect can be produced by saturating the electrolyte with carbon dioxide, although to a less extent. When there is free evolution of hydrogen at the cathode, the contraction is slight; the surface of the deposit is bright and metallic, but under the microscope it has a scaly appearance. When the evolution of hydrogen is small, the deposit shows a greater contraction and it has a brown appearance. The inner structures of the different deposits are practically identical when examined microscopically. The size of the particles is from 1·4 to 2·2 $\mu$, the larger particles generally appearing when an alternating current is used. It is concluded therefore that the contraction is purely a surface phenomenon, due to the aggregation of particles, originally deposited in a highly disperse form, into particles of larger size.

Deposits obtained with direct current were brittle, those from sulphate solutions less so than those from chloride; those obtained with alternating current were flexible. There seemed, however, to be no relation between brittleness and the contraction phenomenon. The brittleness is probably due to the presence of hydrogen in the metal.

II. The superposition of the alternating current causes a lowering of the cathode potential more or less parallel with the lessening of the contraction effect in the deposit. A number of observations, however, indicate that the relation is not so close as might appear to be the case between the structure and contraction of the deposit on the one hand and the deposition potential on the other. Since, however, the contraction takes place almost instantaneously, it is not possible to observe the structure of the metal as it is originally deposited with a high cathode potential. There is no doubt that hydrogen is the important factor influencing both the polarisation and the structure of the deposit. E. H. R.

**New Hydrate of Uranyl Nitrate.** FRANK E. E. GERMANN (*J. Amer. Chem. Soc.*, 1922, **44**, 1466—1469).—The density of solutions of uranyl nitrate has been determined at 24° for compositions up to 50% and a density curve plotted which exhibits a strong curvature towards the composition axis. Cooling and heating curves have been constructed, and both show the existence of an *icositetrahydrate* of uranyl nitrate, $UO_2(NO_3)_2,24H_2O$ This compound forms spontaneously at $-35°$ and exists only below $-20°$. The existence of five distinct fluorescence spectra due to uranyl nitrate as stated by Howes (*Physical Rev.*, 1915, **6**, 192) has been disproved. These are due to the hexahydrate, the icositetrahydrate, and various mixtures of the two depending on the concentration and rate of cooling. J. F. S.

**Complex Uranyl Hypophosphites.** ARTHUR ROSENHEIM and GERT TREWENDT (*Ber.*, 1922, **55**, [*B*], 1957—1960).—The analogy between sulphites and hypophosphites is illustrated furthe by the isolation of alkali uranyl hypophosphites which correspon in their composition with the alkali uranyl sulphites, $R_2[(UO_2)_2(SO_3)_3$ and $R_2[(UO_2)_4(SO_3)_5],xH_2O$, described by Kohlschütter (A., 1900 ii, 484).

*Uranyl hypophosphite*, $UO_2(H_2PO_2)_2$, microcrystalline, yellow prisms, is prepared by agitating solutions of one molecular pro portion of uranyl nitrate and four molecular proportions of sodium hypophosphite (a microcrystalline, pale yellow *trihydrate* is als described); it is almost insoluble in water, but readily solubl in an excess of sodium hypophosphite or uranyl nitrate solution It is transformed by a solution of sodium hypophosphite (4 mole cular proportions) into the *salt*, $Na[(UO_2)_2(H_2PO_2)_5],4{\cdot}5H_2O$, slender pale yellow needles (a *hexahydrate* is also described); the corre sponding anhydrous *potassium* salt, yellow crusts, and *ammonium* salt, pale yellow leaflets, and the *dihydrated guanidinium* salt aggregates of needles, were analysed. Uranyl hypophosphite is converted by six to eight molecular proportions of sodium hypophosphite into the *salt*, $Na[(UO_2)(H_2PO_2)_2],3{\cdot}5H_2O$, large rectangular plates (the *pentahydrate* is also described). Attempt to prepare corresponding compounds with other alkali hypophos phites yielded salts of the series $R[(UO_2)_2(H_2PO_2)_5]$. The compound from uranyl hypophosphite and ten or more molecular proportion of alkali hypophosphite could not be caused to crystallise. H. W.

**The Isotopes of Tin.** F. W. ASTON (*Nature*, 1922, **109** 813).—An immediate result of the application of a method fo increasing the sensitivity of photographic plates towards positive rays has been the definite proof of the complex nature of tin (cf A., 1921, ii, 474). By using tin tetramethyl, eight lines corre sponding approximately with atomic weights 120, 118, 116, 124 119, 117, 122, 121 (in decreasing order of intensity) were definitel proved to be due to tin. The average atomic weight, in proportion to the intensities, agrees well with the accepted value. It i remarkable that the differences between the lines are integral t the highest accuracy, but the lines themselves compared with known lines give atomic weights always tending to be 2 or 3 parts pe 1000 too light for the above whole numbers. It is strongly indicated that this divergence cannot be due to experimenta error. The presence of the two faint components of xenon 128 and 130 previously suspected has now been confirmed. A. A. E.

**Complex Mixed Antimony Iodobromides.** A.-CH. VOURNAZOS (*Compt. rend.*, 1922, **175**, 164—167).—An acid containing the complex anion $-SbI_3Br$ is obtained by the action of dry gaseous hydrogen bromide on antimony tri-iodide in a non-aqueous medium such as glacial acetic acid. It cannot be isolated in a solid state by the evaporation of the acetic acid solution, as, owing to dissociation, only a residue of the tri-iodide remains. The salts

f this acid are, however, obtained in crystalline form by triturating nd finally warming equimolecular proportions of antimony tri- ɔdide and a bromide with a suitable non-aqueous medium, acetic .cid, xylene, etc. The compounds form coloured crystals, which ɩre rapidly decomposed by water or ethyl alcohol, giving anti- nonious oxide, hydriodic acid, and the metallic bromide. *Sodium ɩntimoniodobromide*, $SbBrI_3Na$, prepared in xylene, forms small, ɔrange-yellow crystals. *Potassium antimoniodobromide*, $SbBrI_3K$, ɩs similar in colour, but the *ammonium* and *lithium* salts are reddish yellow. *Zinc antimoniodobromide*, $ZnSbI_3Br_2$, forms brown, tabular crystals, which are fairly stable and only slowly decomposed by water. G. F. M.

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## Mineralogical Chemistry.

**Haloes and Earth-history. A New Radioactive Element.** J. Joly (*Nature*, 1922, **109**, 517—518 and 578—579).—A description of colourless, spherical, halo-like forms, of average diameter 0·0104 mm., occurring in the Archæan black mica of Ytterby. It is suggested that they may be due to a radioactive element (for which the name "hibernium" is suggested) having an α-ray range in air of 1—1·5 cm. A. A. E.

**The Crystal Structures of Marcasite ($FeS_2$), Arsenopyrite (FeAsS), and Loellingite ($FeAs_2$).** Maurice L. Huggins (*Physical Rev.*, 1922, **19**, 369—373).—Arsenopyrite and loellingite are assumed to have the same general arrangement as marcasite, in which the sulphur atoms are considered to be in pairs, each sulphur atom being linked, by pairs of electrons, to one sulphur and four iron atoms, and each iron atom to six sulphur atoms. A. A. E.

**Minerals from near Oudjda, Morocco.** J. Barthoux (*Compt. rend.*, 1922, **175**, 312—314).—An account is given of crystallised minerals (galena, vanadinite, pyromorphite, wulfenite, cerussite, dolomite, calcite, and aragonite) from a lead mine in dolomitic limestone at Gebel Mahser. L. J. S.

**Babingtonite from Japan.** Manjirô Watanabé (*Amer. J. Sci.*, 1922, [v], **4**, 159—164).—Babingtonite occurs with hedenbergite, garnet, chalcopyrite, magnetite, etc., in a metamorphic contact in the Yakuki mine, province Iwaki. A crystallographic and optical description is given of the material. L. J. S.

**Composition of Aerinite.** J. Orcel (*Compt. rend.*, 1922, **175**, 309—311).—Aerinite from Casserras, Huesca, prov. Aragon, consists of a mixture of a blue, transparent, strongly pleochroic mineral with pyroxene, quartz, and spinel. The first is easily separated

by reason of its ready solubility in acids. Analysis of hydrochlo acid solution gave :

| $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | MnO. | CaO. | SrO |
|---|---|---|---|---|---|---|---|---|
| 39·26 | 0·49 | 19·80 | 7·13 | 1·35 | 3·52 | 0·03 | 9·08 | 0·2 |

| $P_2O_5$. | V. | Alkalis. | $H_2O$ (at 106°). | $H_2O$ (at 400°). | $H_2O$ (400° to 1100°). | Total |
|---|---|---|---|---|---|---|
| 0·07 | trace | trace | 5·43 | 11·03 | 2·92 | 100·3. |

corresponding approximately with

$$6SiO_2,2(Al,Fe)_2O_3,(Fe,Mg)O,1\tfrac{1}{2}CaO,7H_2O+3Aq.$$

The mineral represents a new calcium-bearing type of the lept chlorites; this is supported by optical characters and its b haviour when heated. Spectroscopic analysis shows that t strontium and vanadium are present only in the hydrochloric ac extract of the mineral. The cause of the blue colour is discusse it is regarded to be dependent on the molecular structure.

L. J. S.

## Analytical Chemistry.

**Nephelometry of Coloured Hydrosols.** H. Bechhold a F. Hebler (*Kolloid Z.*, 1922, **31**, 7—12).—In the nephelomet investigation of white turbidities it has been repeatedly sho that a strict proportionality exists between the concentration the substance causing the turbidity and the amount of diffract light, provided that no change occurs in the original substan It is now shown that in the case of coloured sols and turbidit *very marked deviations from this proportionality occur.* Co centrated coloured sols such as colloidal indigotin and silver beha in comparison with dilute solutions as though they were less co centrated. This is shown to be due to the absorption of light the coloured particles forming the turbidity. This action in t case of white particles is not great, but in that of coloured partic it is very strong. The disproportionality in the absorption caused particularly by those wave-lengths which are absorbed the turbid medium to a larger or smaller extent. This select absorption must therefore be removed by the use of suitable lig filters. The most efficient filters are shown to be isochroma filters, that is thin layers composed of the substance under inves gation. These filters may be employed either as solutions or dry gelatin films between the source of light and the nephelomet In this way it is possible to investigate nephelometrically colou turbidities and coloured hydrosols in exactly the same way colourless turbidities, and in these circumstances they show exac same proportionality between concentration and amount scattered light as white turbidities. J. F. S

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**estigation, by Means of the Hydrogen Electrode, of :hemical Reactions involved in Water Purification.** GREENFIELD and A. M. BUSWELL (*J. Amer. Chem. Soc.*, **44**, 1435—1442).—Titration curves have been prepared, the hydrogen electrode, for the neutralisation of the car- es of sodium, magnesium, and calcium with a strong acid. ıhown that the shape and position of the curve are unaffected e metallic ion, but that the inflection point occurs at a slightly r Sörensen value in dilute solutions than in the more con- ıted solutions. Precipitation curves of the precipitation of esium hydroxide have been plotted, and these show that the ɔitation of magnesium is complete at a Sörensen value in the bourhood of $P_H=10{\cdot}6$. Magnesium hydroxide does not form the value is as high as $P_H=9{\cdot}0$. Precipitation curves for the pitation of calcium as carbonate, whilst not as regular as ; obtained in the case of magnesium, tend to show that the ion is complete, sufficient carbonate being present at $P_H=9{\cdot}5$. ıinium hydroxide is shown to start precipitating in solutions id as $P_H=4$, and to be completely precipitated at $P_H=6{\cdot}5$—$7{\cdot}5$. 'alues much higher than this, resolution commenced to take ;, and this was complete at a value between $P_H=10$ and =11. The precipitation reactions were not instantaneous, but several hours to reach completion. This was the more noticeable more dilute the solution. J. F. S.

**odium Sulphide as a Substitute for Hydrogen Sulphide Qualitative Analysis.** GIORGIO VORTMANN (*Boll. Sci. tecn.* No. 5; *Giorn. Chim. Ind. Appl.*, 1921, **3**, 565).—A solution in rochloric acid is oxidised, treated with solid sodium carbonate ılight excess, warmed with sodium hydroxide solution (boiled 'emove ammonia if necessary), and precipitated with excess of 0% solution of sodium sulphide. The precipitate (i) may con- ı silver, copper, bismuth, cadmium, lead, iron, cobalt, nickel, nganese, and zinc as sulphides; uranium, chromium, and rare ths as hydroxides; barium, strontium, calcium, and magnesium carbonates; whereas the filtrate (i) may contain the sulphides mercury, nickel, arsenic, antimony, tin, gold, platinum, molyb- ıum, tungsten, and vanadium. On treatment of the precipitate with dilute hydrochloric acid, iron, manganese, zinc, uranium, 'omium, barium, strontium, calcium, magnesium (phosphate), ıium, and rare earths pass into solution (ii), whilst silver, copper, muth, cadmium, lead, cobalt, and nickel remain undissolved (ii). lution (ii) is boiled to remove hydrogen sulphide, and bromine water :hen added, followed by sodium carbonate in excess. The filtrate ) may contain chromium, uranium, and manganese, whilst the ecipitate (iii) contains iron, manganese, zinc, barium, strontium, cium, magnesium, and lithium. After redissolution of the pre- itate (iii) in hydrochloric acid, iron is precipitated with sodium ;tate, manganese with ammonium hydroxide and bromine water, :ium, strontium, and calcium with ammonium carbonate, the c in the filtrate with sodium sulphide, and finally the magnesium

and lithium. The filtrate (i) is boiled with ammonium chloride to precipitate mercury, nickel, and aluminium, whilst antimony, tin, arsenic, molybdenum, tungsten, and vanadium remaining in solution can be separated by known methods. The alkali metals are tested for in another portion of the substance.

CHEMICAL ABSTRACTS.

**Titration of Acids and Bases.** J. L. LIZIUS and N. EVERS (*Analyst*, 1922, **47**, 331—341).—The theory of titration and the dependence of the hydrogen-ion concentration of the end-product on the nature of the salt formed is explained. A list of newer indicators with their colour changes and the $P_H$ range over which they are applicable is given, and four mixed indicators are suggested. A table of common titrations with the hydrogen-ion concentrations at their end-points, suitable indicators, and the colours obtained at their end-points is also given. By titrating to a definite shade of colour instead of to the colour-change of the indicator, an increase in the accuracy of titrations results, and certain titrations are made possible which are impracticable by ordinary methods. H. C. R.

**Symmetrical Diphenylguanidine as a Standard in Acidimetry and Alkalimetry.** C. A. CARLTON (*J. Amer. Chem. Soc.*, 1922, **44**, 1469—1474).—The suitability of symmetrical diphenylguanidine as a standard in acidimetry and alkalimetry has been investigated. It is shown that this substance can easily be obtained in a sufficiently high state of purity for the present purpose by three recrystallisations of the crude material from toluene. The pure compound is stable in air and soluble in alcohol. It may be titrated directly in cold solutions with either an alcoholic or an aqueous solution of hydrochloric acid, using either bromophenyl-blue or methyl-red as indicator. The results obtained with this substance are comparable with those obtained with sodium carbonate or silver chloride, and diphenylguanidine is more convenient in use. Diphenylguanidine is the only basic substance, proposed as a standard, which meets all the requirements of an ideal standard. J. F. S.

**Micro-incineration.** A. SCHOELLER (*Ber.*, 1922, **55**, [*B*], 2191—2192).—The substance under investigation is spread evenly over a thin strip of glass (5—6 mm. wide) which is placed in a horizontal hard glass tube about 10 mm. in diameter and 12 cm. long. The tube is heated very gently until all volatile matter is expelled. The residue is allowed to cool and is subsequently heated rather more strongly in a current of moist oxygen; in most cases, the carbon disappears rapidly without at any time glowing. With difficultly combustible substances it is advisable to interrupt the heating again. Too powerful ignition is to be avoided. The minutest trace of ash is readily visible under the microscope. The method is particularly suitable for the incineration of sections of plant-tissue, since the original structure is better preserved than when they are heated over a free flame.

H. W.

**The Estimation of Hydrogen and its Separation from Gaseous Paraffins by means of Palladious Chloride.** J. A. MULLER and A. FOIX (*Bull. Soc. chim.*, 1922, [iv], **33**, 713—717).—Hydrogen may be separated from gaseous paraffins and estimated by its reducing action on excess of palladious chloride. The precipitated palladium is dried and weighed, and hence the quantity of hydrogen is calculated. A correction should be made for the small quantity of the gas occluded in the metal; the authors state that 1 mg. of palladium represents 0·24 c.c. of hydrogen measured at 0° and 760 mm. when the reaction takes place under the prescribed conditions. H. J. E.

**Electrometric Titrations with Mercury Perchlorate.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 332—343).—Chlorides, bromides, or iodides may be titrated with mercury perchlorate solution, the end-point of the titration being determined with accuracy by electrometric means even in very dilute solutions, but the method cannot be applied to mixtures of these salts. The method is also trustworthy in the case of thiocyanates, cyanides, ferrocyanides, formates, acetates, monochloroacetates, lactates, benzoates, and salicylates, but it cannot be used for trichloroacetates owing to the ready hydrolysis of the mercury compound, or for the salts of polybasic aliphatic acids. The mercury perchlorate solution is prepared by saturating perchloric acid with mercuric oxide. W. P. S.

**Detection of Fluorine.** B. FETKENHEUER (*Wiss. Veröffentl. Siemens-Konzern,* 1922, **1**, [3], 177).—The substance is heated with sand and a few c.c. of sulphuric acid at 90° in a test-tube. On shaking the tube, the presence of fluorine is shown by the acid collecting into oily drops, which appear not to wet the surface of the glass. With 2 grams of substance, 0·01% of fluorine may be detected after heating for one minute. Insoluble fluorides such as aluminium fluoride must first be fused with sodium carbonate and sand; the fused mass is then heated as above with sulphuric acid. A. R. P.

**The Colour of Iodine Solutions at Low Temperature.** JEAN PICCARD and E. HERRMANN (*Helv. Chim. Acta,* 1922, **5**, 625—626).—The brown colour formed by iodine in solvents containing oxygen has been suggested as a qualitative test for oxygen (this vol., *ii*, 389), in absence of other elements or groups of an unsaturated character such as tervalent nitrogen. It has been observed that very dilute solutions of iodine in hydrocarbons such as light petroleum, which are violet at the ordinary temperature, become brown at lower temperatures, in the neighbourhood of −20°. When the iodine concentration is increased beyond a certain value, about 1 mg. in 10 c.c., however, the colour change does not take place. It is shown that the brown colour is due to an impurity in the commercial light petroleum, and that it does not appear with carefully purified specimens. The phenomenon can be reproduced by addition of a small quantity of alcohol to

*the pure light petroleum, or to toluene,* chloroform, and other solvents. E. H. R.

**Rapid Estimation of Sulphur.** Luigi Losana (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 297—299).—The method previously described (this vol., ii, 582) gives accurate results with pyrites, copper pyrites, and other mineral sulphides, ultramarine, adulterated white lead, cement, various rocks, sulphates of copper, sodium, etc., naphtha, anthracene, coke, ichthyol, "saccharin," ebonite, and caoutchouc. T. H. P.

**Determination of Sulphur in Vulcanised Rubber.** J. W. W. Dyer and Amy R. Watson (*J. Soc. Chem. Ind.*, 1922, **41**, 251—252).—*Methods are described for the estimation of free and* combined sulphur in vulcanised rubber. These are as follows. (*a*) Combined sulphur. The sample (0·5—3·0 grams) is added to 30—40 c.c. of nitric acid (*d* 1·42) in a suitable flask and the reaction started by gentle heating; subsequently the mixture is heated to the boiling point and boiling continued until the liquid is clear. Pure powdered potassium permanganate is now added, about 0·25—0·5 gram at a time, and the heating continued between additions. The addition of permanganate is continued until finally a small black precipitate *remains; this requires generally* about 2 grams of permanganate. The contents of the flask are poured into a dish and evaporated to dryness, taken up with 10 c.c. of concentrated hydrochloric acid, and again evaporated to dryness. The residue is treated with water, made up to 100 c.c., and made *just acid to methyl-orange at the boiling point.* The sulphur is then precipitated as barium sulphate. (*b*) Free sulphur. To 50—60 c.c. of acetone, 0·5—1 gram of material is added and the free sulphur extracted. To the extract 0·5—1 gram of powdered permanganate is added, the mixture *shaken, and kept at the ordinary temperature for thirty minutes. If the purple colour* disappears a little more permanganate is added. The acetone is then distilled off on the water-bath and the brown residue heated at 100—110° for a short time. About 3—5 c.c. of hydrochloric *acid (d 1·16) is added for each gram of permanganate used, and the solution heated until colourless. It is then diluted a little and* filtered, the filtrate is made up to 100 c.c., and ammonia cautiously added until the solution becomes yellow and slightly turbid. It is then made just acid and precipitated while boiling with 4—5 c.c. *of N/2-barium chloride solution.* Both methods give results which are in good agreement with those obtained by the Carius method. J. F. S.

**Quantitative Micro-analysis of Mixtures with Special Reference to Organic Ultimate Analysis.** A. Benedetti-Pichler (*Z. anal. Chem.*, 1922, **61**, 305—331).—The author describes the advantages of micro-chemical methods, points out *the importance of obtaining representative samples in dealing* with very small quantities of substances, and gives instances of the application of the methods and their limits of accuracy. W. P. S.

**Volumetric Estimation of Carbon and Hydrogen in Organic Compounds.** JOSEF LINDNER (*Ber.*, 1922, **55**, [*B*], 2025—2031).—The substance is burnt in the usual manner and the products of its combustion are passed over a substance which by its hydrolysis gives hydrogen chloride and thence into a known volume of standard barium hydroxide solution. The latter is titrated with *N*/10-hydrochloric acid in the presence of phenolphthalein; the carbon dioxide is subsequently removed after addition of an excess of hydrochloric acid and the resulting solution is again titrated with barium hydroxide. With *N*/10-solutions and burettes of 50 c.c. capacity, the analysis is conveniently performed with 20 mg. of material.

The most suitable substance for hydrolysis is chloronaphthyloxychlorophosphine, which may contain chloronaphthyltetrachlorophosphine: it is decomposed by water in accordance with the equations:

$$C_{10}H_6Cl{\cdot}PCl_4+H_2O=C_{10}H_6Cl{\cdot}POCl_2+2HCl;$$
$$C_{10}H_6Cl{\cdot}POCl_2+2H_2O=C_{10}H_6Cl{\cdot}PO(OH)_2+2HCl;$$
$$C_{10}H_6Cl{\cdot}PO(OH)_2+C_{10}H_6Cl{\cdot}POCl_2=2C_{10}H_6Cl{\cdot}PO_2+2HCl.$$

It is prepared by passing chlorine into molten naphthyldichlorophosphine until three atomic proportions of the gas have been absorbed. It is not a well-defined individual. Hydrogen chloride is freely and quantitatively evolved when a current of moist air is passed through the molten material. It is, however, convenient to depress its melting point to some extent by a preliminary regulated treatment with moist air. The material prepared in this manner somewhat readily evolves considerable amounts of readily volatile acid products, which must be removed by protracted exposure to a current of dry air; the elimination of acid is thereby ultimately reduced to a small amount, for which a correction can be applied, but the presence of the acid has the drawback that the sharpness of the end-point in the ultimate titration is diminished.

Test analyses show that the method gives accurate results, which, however, are somewhat low for hydrogen, the source of error most probably lying in the uncertainty of the correction for the acidic products evolved spontaneously from the phosphorus compound. H. W.

**Absorption of Carbon Monoxide by Acid Cuprous Chloride Solution in the Presence of a Reducing Agent.** ALFRED KROPF (*Z. angew. Chem.*, 1922, **35**, 451—452).—The rate of absorption of carbon monoxide by acid cuprous chloride solution is increased by the addition of stannous chloride to the solution. The stability of the solution is improved by the use of a slight excess of stannous chloride (cf. Krauskopf and Purdy, A., 1920, ii, 267). J. S. G. T.

**Comparison of Colorimetric and Electrometric Estimations of Hydrogen-ion Concentrations in Solutions containing Carbon Dioxide.** GLENN E. CULLEN and A. BAIRD HASTINGS (*J. Biol. Chem.*, 1922, **52**, 517—520).—Contrary to the

results obtained by Evans (A., 1921, ii, 271), the colorimetric and electrometric methods for the estimation of the hydrogen-ion concentration of solutions containing carbon dioxide yield identical results, provided precautions are taken to prevent the loss of carbon dioxide. E. S.

**Estimation of Small Amounts of Potassium by the Lindo-Gladding Method.** WILLIAM HAZEN (*J. Assoc. Off. Agric. Chem.*, 1922, **5**, 456—460).—In the estimation of potassium by the Lindo-Gladding method, the use of 90% alcohol for washing gives better results than 80% alcohol, and when working with small amounts of potassium salts and high accuracy is desired, it is advisable to use the stronger alcohol for washing after the ammonium chloride treatment as well. The lower results obtained by using the weaker alcohol do not appear to be due to the sodium salts which may be present, as has been suggested, as equally low results are obtained in the absence of sodium salts. As, however, it takes a longer time to wash out the ammonium salts with 90% alcohol, it is preferable to use 80% alcohol for the second washing in ordinary fertiliser work, where the percentage error arising from this will not be very serious, as the samples generally contain relatively high amounts of potassium. G. F. M.

**Identification of Cæsium and Rubidium.** JOHN MISSENDEN (*Chem. News*, 1922, **124**, 362).—The spectroscope affords the best means of distinguishing cæsium from rubidium; the former shows two bright blue lines (4557 and 4592) in the blue portion of the spectrum, whilst rubidium has two lines (4200 and 4237) in the violet and two other lines (7953 and 7810) in the red. The salts of the two metals resemble each other generally, but there is a considerable difference in the solubility of the two nitrates; 100 parts of water at 3·35° dissolve 11 parts of cæsium nitrate and 79·9 parts of rubidium nitrate. W. P. S.

**Hydrotimetric Precision and Aqueous Preparation of the Standard Soap Solution.** ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1922, **26**, 18—21).—Clark's method as modified by Boutron and Boudet is used, but a standard soap solution of only one-tenth the strength is recommended. It is prepared by dissolving 3·5 grams of white Marseilles soap in 200 c.c. of boiling water and then making the volume up to 900 c.c. This solution is diluted, if necessary, until 24 c.c. of it corresponds exactly with 40 c.c. of a 0·025% solution of calcium chloride or of a 0·059% solution of barium nitrate. W. G.

**Estimation of Calcium in Natural Phosphates.** R. MEURICE (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 198).—The phosphate is treated with mineral acid, the silica removed, and iron and aluminium removed as phosphates. The filtrate is neutralised with ammonia, treated with 20 c.c. of 20% hydrochloric acid, and 30 c.c. of 4% ammonium oxalate. The solution is warmed and 10% ammonium acetate solution added at a rate of about 30 drops per minute. A granular precipitate of calcium oxalate

is thus obtained, and is collected, washed, and ignited as usual. Test analyses carried out on known quantities of calcium in the presence of large excess of phosphate and magnesium sulphate gave very accurate results. H. C. R.

**Estimation of Magnesium and Alkalis in Minerals.** L. H. Borgström (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 118—123).—The precipitation of magnesium hydroxide is best effected with piperidine, a little of which should also be added to the washing water. Lawrence Smith's method for the separation of magnesium from alkalis in silicate analysis is the most satisfactory.

Chemical Abstracts.

**Colorimetric Method for the Estimation of Small Amounts of Magnesium.** A. P. Briggs (*J. Biol. Chem.*, 1922, **52**, 349—355).—The method described is similar to that of Hammett and Adams (cf. this vol., ii, 587). E. S.

**Estimation of Magnesium in Blood, Plasma, and Serum.** W. Denis (*J. Biol. Chem.*, 1922, **52**, 411—415).—The method is essentially the same as that of Briggs (preceding abstract) and of Hammett and Adams (this vol., ii, 587). E. S.

**Magnesium Compound of 8-Hydroxyquinoline.** Carl Th. Mörner (*Pharm. Zentr.-h.*, 1922, **63**, 399—402; cf. Griebel, A., 1921, ii, 606).—If an aqueous solution of 8-hydroxyquinoline (sulphate) is treated with a suspension of magnesium hydroxide, the latter goes into solution and a lustrous, sulphur-yellow precipitate of the magnesium compound of 8-hydroxyquinoline is formed. The precipitate is also given by "magnesia mixture." The precipitate is microcrystalline and consists of hexagonal platelets. The reaction takes place only in alkaline solution and is sufficiently sensitive to detect 1 part of magnesium in 25,000. The precipitate contains 6·25—6·29% of magnesium and approximates to the formula $(C_9H_6ON)_2Mg,4H_2O$. The compound is also formed by the action of 8-hydroxyquinoline on magnesium ammonium phosphate. The reaction thus permits the separation of magnesium from phosphate in ammoniacal solution. Its use as a dry antiseptic is suggested. G. W. R.

**Lead. I. Estimation of Minute Amounts of Lead in Biological Material.** L. T. Fairhall (*J. Ind. Hyg.*, 1922, **4**, 9—20).—The ash is dissolved in dilute hydrochloric acid, the solution neutralised to methyl-orange with sodium hydroxide, and then slightly acidified with hydrochloric acid. Lead is precipitated as sulphide, the washed precipitate dissolved in 2—5 c.c. of concentrated nitric acid, and boiled to expel hydrogen sulphide. After neutralising with sodium hydroxide and slightly acidifying with acetic acid, an excess of potassium chromate is added, and the solution boiled. The precipitate is dissolved in hydrochloric acid, and an excess of potassium iodide is added to the solution, which is titrated with 0·005*N*-sodium thiosulphate solution. For biological materials, the method appears to be accurate to ±3%.

Chemical Abstracts.

**Colorimetric Estimation of Manganese in Steels, Alloys, and Ores.** J. HESLINGA (*Chem. Weekblad*, 1922, **19**, 302—303).—The ordinary method of oxidising to permanganate in acid solution is unsatisfactory when iron is present, because of the yellow colour of iron salts. A simple and accurate estimation may be made by employing the compound $H_2MnO_3$, which in alkaline solution gives a yellowish-brown to dark brown coloration.

One hundred to 200 mg. of material are dissolved in a suitable acid, and the solution is diluted and treated with excess of powdered zinc oxide, made up to 100—200 c.c., and filtered. The zinc oxide precipitates the tervalent metals and copper completely after a few minutes' shaking at the ordinary temperature. The filtered solution is poured into a burette, and allowed to fall into a solution containing hydrogen peroxide (3%) and excess of potassium hydroxide (10%) until a suitable colour is obtained; this is matched by means of a standard manganese solution. Several titrations are carried out in succession, adding more of the unknown solution, and matching the colour by means of the standard. Addition of only 0·02 mg. of manganese is easily detected.

Lead does not interfere if excess of potassium hydroxide is employed; if nickel and/or cobalt are present, potassium cyanide is added during the titration. Accurate results are readily obtained when the manganese content is not greater than 20%. S. I. L.

**Estimation of Chromium in Metals.** WILLI LÖFFELBEIN (*Chem. Ztg.*, 1922, **46**, 679).—Chromium is estimated in nickel bronzes and similar alloys by removing the heavy metals from a solution of the alloy with hydrogen sulphide, treating the oxidised filtrate with a slight excess of ammonia, collecting, igniting, and fusing the precipitate with sodium peroxide, acidifying the filtered solution of the melt with hydrochloric acid, adding potassium iodide, and titrating the liberated iodine with sodium thiosulphate solution. A. R. P.

**Rapid Method for the Estimation of Chromium in Nickel-Chromium Steel.** WILHELM HILD (*Chem. Ztg.*, 1922, **46**, 702—703).—The chromium is oxidised to chromic acid in a sulphuric acid solution of the steel by means of potassium permanganate, the excess of which is destroyed with manganese sulphate. The chromic acid is then estimated by addition of an excess of standard ferrous sulphate solution and titration with permanganate or dichromate [cf. *J. Soc. Chem. Ind.*, 1922, **41**, 671A.] A. R. P.

**Estimation of Small Amounts of Molybdenum in Tungsten.** DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 1462—1465).—Small amounts of molybdenum may be estimated in tungsten by converting the molybdenum into xanthate, extracting this with chloroform, and converting into sulphide and oxide. The method consists in dissolving 1 gram of the sample in a mixture of nitric and hydrofluoric acids and evaporating with sulphuric acid. The yellow oxides are dissolved in sodium hydroxide solution and trans-

ferred to a 200 c.c. separating funnel, acidified with sulphuric acid, and the solution diluted so that 1 c.c. contains about 0·1 mg. of molybdenum. The volume is then made up to 150 c.c., 0·5 gram of potassium xanthate and a few drops of 1 : 3-sulphuric acid are added and the mixture is shaken thoroughly. About 10 c.c. of chloroform are then added and the whole is shaken for several minutes. The highly-coloured chloroform layer settles at the bottom and is run into a second funnel for washing. The original solution is repeatedly treated with potassium xanthate, acid, and chloroform until the chloroform layer is colourless, each portion of chloroform solution being added to the first. The chloroform solution of molybdenum xanthate is washed with water several times, run into a 150 c.c. beaker, and evaporated to dryness. The residue is heated and converted into a mixture of oxide and sulphide. This is dissolved in nitric acid, evaporated with sulphuric acid, and precipitated as molybdenum sulphide by passing hydrogen sulphide into the hot molybdenum solution made alkaline with sodium hydroxide. The solution is then slowly acidified with dilute sulphuric acid and the precipitate filtered, washed with hot water, and carefully ignited to oxide. The results are easily reproducible and trustworthy, and the method is good for mixtures containing small amounts of molybdenum. J. F. S.

**Rapid Analysis of Ferro-tungsten.** LUIGI LOSANA and ENRICO CAROZZI (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 299—301).—Ferro-tungsten is readily dissolved in 50% nitric acid solution containing a little hydrofluoric acid, subsequent treatment with concentrated sulphuric acid resulting in the elimination of the hydrofluoric acid and precipitation of the tungsten as tungsten trioxide, which may be either weighed as such or estimated volumetrically (cf. *J. Soc. Chem. Ind.*, 1922, **41**, 671A). T. H. P.

**Electrometric Titration of Uranium with Potassium Permanganate and Potassium Dichromate.** D. T. EWING and E. F. ELDRIDGE (*J. Amer. Chem. Soc.*, 1922, **44**, 1484—1489).—When solutions of uranyl sulphate, reduced with zinc, are titrated electrometrically with potassium permanganate or when solutions of uranium chlorides similarly reduced are titrated with potassium dichromate, a change in the oxidation potential occurs when the tervalent uranium is all oxidised to the quadrivalent condition, and a second change occurs when the latter is all oxidised to the sexavalent condition. Thus the total amount of uranium may be calculated. A third change of potential is observed when iron is present, and this represents the point where all the ferrous iron is converted into ferric iron. The determination is carried out with apparatus of the usual type, except in the form of the titration vessel, since it is necessary to prevent the free access of air. The titration cell is a glass vessel fitted with a cover which has six holes bored in it. Through the holes pass a tube for leading in carbon dioxide, a platinum electrode, the connecting tube of a calomel cell, a stirrer fitted with a mercury seal, the tip of the burette, and the mouth of a Jones reductor. All the tubes passing

through the cover are fitted tightly. The method of procedure adopted is as follows: (a) *Estimation of uranium by permanganate.* Ten c.c. of a solution of uranium as sulphate (containing about 0·013 gram $U_3O_8$ per c.c.) are added to 40 c.c. of sulphuric acid solution *A* (2 c.c. conc. acid, 88 water) and warmed at 80—90°. Carbon dioxide is passed through the titration cell to remove the air, and the uranium solution slowly passed through the Jones reductor into the cell, the reductor being finally rinsed with 50 c.c. of sulphuric acid *A*. The final solution at this stage has a volume of 100 c.c., contains 2 c.c. of concentrated sulphuric acid, and is brown. The stirrer is set in motion and the permanganate slowly added. The *E.M.F.* rises slowly at first and then jumps to a steady value which represents the point at which all the tervalent uranium has been converted into the quadrivalent condition and the solution has become green. Continued addition of permanganate does not affect the *E.M.F.* noticeably until the second end-point is reached, and here the *E.M.F.* jumps rapidly. At this point, the whole of the quadrivalent uranium has been converted into the sexavalent condition. The volume of permanganate used between the first and second end-points is equal to the theoretical amount of oxidising agent required to oxidise uranium from the quadrivalent to the sexavalent condition. Hence from this quantity the total amount of uranium present, no matter what its state of oxidation provided that none of it is sexavalent, can be calculated. (b) *Estimation of uranium and iron with permanganate.* The process is carried out as above; the first and second end-points give, as before, the quantity of uranium. After the uranium has all been oxidised to the sexavalent condition, the oxidation of the ferrous iron commences and when this has been completed the third end-point is observed. Hence the volume of permanganate required to carry the *E.M.F.* from the second to the third end-point is equivalent to the amount of iron present. (c) *Estimation of uranium by dichromate.* The process is carried out exactly as in the first case, and two end-points are obtained which have the same significance as in the other cases, but the slope of the second end-point is not so clear as in the other cases. All methods yield excellent results. J. F. S.

**The Estimation of Small Quantities of Gold as Colloidal Gold by the Colorimetric Method.** J. A. Muller and A. Foix (*Bull. Soc. chim.*, 1922, [iv], **33**, 717—720).—Small quantities of gold may be rapidly and accurately estimated colorimetrically after separation from other metals, provided that the concentration of the gold is not greater than 1/40 mg. per c.c., and that the colloidal particles are of the same size in the two solutions to be compared. The latter condition is realised by precipitation in identical circumstances. The presence of vanadium leads to inaccurate results. H. J. E.

**Separation of Palladium and Platinum by means of Dimethylglyoxime.** C. W. Davis (*U.S. Bur. Mines, Repts. Investigations*, 1922, No. 2351).—The weighed metals are dis-

solved in a little aqua regia, the solution is evaporated to dryness, the residue moistened with a drop of hydrochloric acid, diluted with cold water, and dimethylglyoxime added with constant stirring until no further precipitate is formed. After keeping for a few minutes, the voluminous precipitate is collected on a filter, well washed with cold water, and ignited, first in air and finally in hydrogen to obtain pure palladium. The method was tested with quantities of each metal ranging from 0·15 to 11 mg., and the greatest divergence in five analyses was 0·03 mg.

CHEMICAL ABSTRACTS.

**A Micro-modification of Benedict's Method for the Estimation of Reducing Sugar in Urine.** MILLARD SMITH (*J. Lab. Clin. Med.*, 1922, **7**, 364—368).—The modification, like the original method, is applicable only to urines containing not less than 0·17% of sugar. Exactly 1·0 c.c. of Benedict's solution is run from a pipette into a special test-tube, 0·2—0·7 gram of anhydrous sodium carbonate is added, and a pebble or piece of quartz. Urine is slowly added to the mixture, maintained at the boiling point, from a Mohr pipette, graduated to read directly the percentage of sugar present. CHEMICAL ABSTRACTS.

**Critical Study of Bang's Method for the Estimation of Reducing Substances in Blood.** HENRI LABBÉ, F. NEPVEUX, and MÉNÉLAS NOMIDIS (*J. Pharm. Chim.*, 1922, [vii], **26**, 49—63).—Bang's micro-titrimetric method for the estimation of reducing sugars in blood, consisting in oxidising with iodic acid the cuprous oxide produced by reduction by about 100 mg. of the blood absorbed in blotting paper and clarified, and estimation of the excess of iodic acid by titration with thiosulphate in presence of an alkali iodide, gives satisfactory results provided the following points are attended to. All the reagents used must be absolutely pure. Notably the potassium chloride and uranium acetate used for preparing the clarifying solution should be specially purified, and the iodate is preferably prepared by oxidising potassium iodide with permanganate. Mercuric sulphate, or alcohol, or Patein's reagent was found to give inferior results as clarifying agents, as they all retain a quantity of sugar, and at the same time partly compensate for this by allowing a certain amount of reducing substances originating from the albumin to remain in solution. Bang's reagent exhibits these faults in a much less marked degree. The heating of the clarified blood with the iodate-copper solution should be continued for exactly four minutes, and heating by means of a current of steam generated under constant well-defined conditions in a 1500 c.c. flask containing a constant level of water is to be preferred to direct heating, as experiments showed that the method of heating had a considerable influence on the results. The errors should not on the average exceed 5% if all the above precautions are taken, and the estimation of a large number of samples to which known weights of invert-sugar had been added gave a mean of 97% of the added sugar actually found. G. F. M.

**Acetol. I. A New Test for Carbohydrates.** OSKAR BAUDISCH and HARRY J. DEUEL (*J. Amer. Chem. Soc.*, 1922, **44**, 1585—1587).—The test depends on the production of acetol from carbohydrates. An aqueous solution of the carbohydrate (0·1 gram in 100 c.c.) is treated with solid sodium hydrogen carbonate (5 grams) and distilled nearly to dryness. With the carbohydrates which are more readily attacked, the solution in the distilling flask very quickly turns brown, and the distillate has a sweet odour. The residue in the flask after distillation has a strong typical caramel odour. The distillate is treated with *o*-aminobenzaldehyde (30 mg.) and enough potassium hydroxide solution to give a distinctly alkaline reaction; after addition of a piece of porous plate, it is evaporated over a free flame to about 1/3 volume, cooled, and acidified with hydrochloric acid. Then solid sodium hydrogen carbonate is added until the solution is alkaline to litmus. The presence of acetol is shown by a strong blue fluorescence, which can be seen in daylight, but more readily in light of short wave-lengths such as that yielded by the iron arc. To confirm the test, the 3-hydroxy-2-methylquinoline may be extracted by shaking the solution several times with alcohol-free ether; the ethereal solution is dried with sodium sulphate, and the solvent removed. The colourless, needle-like crystals of 3-hydroxy-2-methylquinoline which remain dissolve readily in a little alcohol, and the fluorescence shows up strongly after the addition of water to the alcoholic solution. The sensitiveness of the reaction has not been determined except for dextrose, with which quantities as small as 5 mg. give a positive result.

The test is shown by arabinose, xylose, ribose, lyxose, dextrose, fructose, mannose, galactose, glucosamine, lactose, sucrose, maltose, and dextrin, but not by acetoacetic acid, glycerol, β-hydroxybutyric acid, lactic acid, starch, or glycogen.

The formation of 3-hydroxy-2-methylquinoline when treated with *o*-aminobenzaldehyde and potassium hydroxide appears to be a specific reaction of acetol; it is not given by pure methylglyoxal, aldol, acetone, acetaldehyde, ethyl acetoacetate, crotonaldehyde, or ethyl alcohol. H. W.

**Estimation of the Cellulose Content of Wood and other Raw Materials by the Action of Chlorine and Carbon Tetrachloride.** E. HEUSER and H. CASSEUS (*Papierfabr., Fest-u. Auslandheft*, 1922, 80—93; cf. A., 1921, i, 708; Frank, D.R.-P. 323936).—1·2 to 1·5 Grams of material of medium fineness are shaken with 50 c.c. of a saturated solution of chlorine in carbon tetrachloride for one to two hours, and the fibre is collected on a filter and washed successively with carbon tetrachloride, alcohol, and water. The lignin chloride is then dissolved out with a 2% solution of sodium sulphite, the residue washed with water, dried, and weighed. The product, which contains 3—3·5% of pentosan and 0·04—0·05% of ash, has a copper number of 0·8—0·91 as compared with 3·14—3·23 by the older method. The yield of pure cellulose was 56%. CHEMICAL ABSTRACTS.

**Estimation of α-, β-, and γ-Cellulose.** OPFERMANN (*Paper*, 1921, **28**, 19—25).—The cellulose content of the pulp is estimated as follows: 10 grams of pulp are covered with 50 c.c. of mercerising liquid (17—18% sodium hydroxide) and allowed to stand for thirty minutes. The fibre mass is then rubbed with 50 c.c. of water, filtered on a Buchner funnel with a fine cotton filter, and carefully sucked dry. The residue is washed with cold water until the wash-water no longer has an alkaline reaction; this usually requires ten to twelve washings, 50 c.c. of water being used each time. Finally, the α-cellulose is washed with hot dilute acetic acid, then with hot water (six to eight times), dried, and weighed. β-Cellulose is estimated by adding concentrated acetic acid to the alkaline filtrate until a marked acid reaction is produced, when β-cellulose separates in a finely divided state, and the colour of the brown filtrate becomes considerably lighter. To assist coagulation, the precipitate is heated on the water-bath at 100° until it settles. It is filtered on a fine cloth filter, washed six to eight times with hot water, transferred to a porcelain dish, dried, and weighed. γ-Cellulose is estimated by difference.

CHEMICAL ABSTRACTS.

**Determination of the Iodine Value of Aliphatic and Aromatic Unsaturated Compounds.** D. HOLDE (*Chem. Umschau*, 1922, **29**, 253—254; cf. this vol., ii, 533).—Attention is directed to the different behaviour of the Hanus reagent with simple aliphatic oils such as sesame oil and mineral oils containing unsaturated cyclic structures. In the first case, even with varying excess of iodine, constant values are obtained, whilst in the second case variable values far above the theoretical are obtained with more or less considerable excess of the reagent. This is due to the rupture of bridge structures, and in certain circumstances the behaviour of an oil with excess of the Hanus reagent can be utilised to determine whether cyclic unsaturated compounds are present. G. F. M.

**The Sulphuric Acid Test for Liver Oils.** J. C. DRUMMOND and A. F. WATSON (*Analyst*, 1922, **47**, 341—348).—The substance present in liver oils which is responsible for the well-known purple coloration with sulphuric acid was found in the following species: Man, horse, ox, pig, cat, monkey, rabbit, guinea pig, chicken, duck, pigeon, rat, mouse, frog, shark, cod, haddock, ling, coal fish, dog fish, sprat, and skate. The substance appears to be a normal constituent of the liver, and is not derived from the bile or from products of autolysis or putrefaction. Evidence is presented to show that it is probably derived from the food, although an examination of the stages in the food of the cod did not reveal its ultimate origin with certainty. The chemical nature of the substance has not been ascertained. It forms a low proportion of the unsaponifiable fraction, is not cholesterol, and probably not a member of the lipochrome pigments. It is thermo-stable in the absence of air or oxygen, but is rapidly destroyed by oxidation. The few properties of the substance which are known, as

well as the available data regarding its distribution in natural products, show certain resemblances to the unidentified dietary unit known as vitamin-*A*; and, without assuming the identity of the two factors, it is suggested that the association may be of some significance. The colour test cannot be regarded as specific for liver fats, although they usually give the most intense reactions. The body fat and fat from other organs of animals, especially if they have been fed on liver oils, may give the reaction.

H. C. R.

**Chemical and Physiological Investigation of the Fats and Lipoids of the Blood. II. The Kumagawa-Suto Method of Estimation of Lipoids.** P. LEMELAND (*Bull. Soc. Chim. biol.*, 1922, **4**, 300—321; cf. A., 1921, i, 633).—In the Kumagawa-Suto method, errors occur which are due to oxidation of the unsaturated acids during the heating and drying processes, and to loss of volatile constituents of the total unsaponifiable matter. The author promises to describe a new technique for the estimation.

E. S.

**Estimation of Small Quantities of Furfuraldehyde Colorimetrically.** PAUL FLEURY and GABRIEL POIROT (*J. Pharm. Chim.*, 1922, [vii], **26**, 87—96).—Small quantities of furfuraldehyde may be estimated colorimetrically with an accuracy of about $\pm 1\%$ by means of the blue coloration which is formed in acidic medium with orcinol in a suitable solvent, preferably acetic acid, and is intensified by the presence of traces of iron. The reagents required are hydrochloric acid (*d* 1·19) containing 20 mg. of iron as ferric chloride per litre; glacial acetic acid containing 1 gram of orcinol in 1600 c.c., and a standard solution of furfuraldehyde containing 1 gram in 10 litres of 1% acetic acid. One c.c. of the standard solution or of the solution to be estimated is mixed with 4 c.c. of the acetic acid-orcinol solution and 5 c.c. of the hydrochloric acid, and warmed for one minute in a water-bath. After keeping for thirty minutes, the maximum coloration is developed, and comparison is made with the standard in a Duboscq colorimeter. The reaction has a sensibility of about 4 mg. of furfuraldehyde per litre.

G. F. M.

**New Analytical Applications of Nessler's Reagent. Characterisation of Ketones; Estimation of Aldehydes.** J. BOUGAULT and R. GROS (*J. Pharm. Chim.*, 1922, **26**, 5—11).—Certain ketones, such as acetone, methyl ethyl ketone, *cyclo*hexanone, trimethyl*cyclo*hexenone, acetophenone, and *p*-methoxyacetophenone, give with Nessler's reagent in the cold a yellowish-white precipitate which dissolves in acid or on the addition of potassium cyanide with liberation of the ketone. This reaction may be used for the detection of acetone in urine, by suspending a small capsule, containing 10 c.c. of Nessler's reagent, over 200 c.c. of urine, previously acidified, the whole being covered by a bell-jar. The time required for the formation of a precipitate varies inversely ure the concentration of the acetone in the urine.

Certain aldehydes react quantitatively with Nessler's reagent according to the equation $R·CHO+H_2O+2I=2HI+R·CO_2H$, the iodine coming from the mercuric iodide. To a known volume of the aldehyde solution, corresponding with 0·01—0·05 gram of the aldehyde, is added an excess (about 30 c.c.) of Nessler's solution, and 10 c.c. of sodium hydroxide solution. The mixture is well shaken, and after some time is neutralised with hydrochloric acid. A known volume of standard iodine solution is added, and then the excess of iodine is titrated back with standard thiosulphate solution. It is necessary to make a control estimation on the sodium hydroxide. Accurate results were obtained with formaldehyde, furfuraldehyde, benzaldehyde, and piperonaldehyde, but the method is uot satisfactory for vanillin or acraldehyde.

W. G.

**The U.S.P. Test for Acetone in Alcohol.** J. W. E. HARRISSON (*J. Amer. Pharm. Assoc.*, 1922, **11**, 16).—Some zinc salts and antimony compounds interfere with the test, which depends on the development of a violet colour in presence of sodium hydroxide and sodium nitroprusside. The best test consists in the addition of 1 c.c. of potassium hydroxide solution to 5 c.c. of the ethyl alcohol, followed by a solution of iodine in potassium iodide until coloration occurs; heat must not be used. A precipitate is obtained immediately if 0·25% of acetone is present.

CHEMICAL ABSTRACTS.

**Analysis of Camphor Preparations.** MAURICE FRANÇOIS and ÉMILE LUCE (*J. Pharm. Chim.*, 1922, [vii], **25**, 500—507).—Tincture of camphor (French Codex) contains 10 grams of camphor dissolved in 90 grams of 90% alcohol, and should have $\alpha$ +6·5° in a 200 mm. tube. The optical rotation varies somewhat with the strength of the alcohol, but, provided that the alcoholic concentration is correct, a lower rotation than that mentioned will indicate a deficiency in the camphor content or that artificial (inactive) camphor is present. The optical rotation of camphor decreases slightly with increase of temperature and in alcoholic solution the value decreases considerably for a decrease in the alcoholic concentration. For instance, in absolute alcohol camphor has $\alpha_D$ +43·0°, and in 90% alcohol $\alpha$ +39·66°. To ascertain whether a low value for the optical rotation of a sample of tincture of camphor is due to deficiency in camphor or to the presence of artificial camphor, 50 c.c. of the sample are evaporated under a bell-jar over sulphuric acid, the crystalline residue is dried for a further forty-eight hours over sulphuric acid, and its optical rotation then determined in alcoholic solution; natural camphor has $\alpha_D$ +43°. The alcoholic strength of tincture of camphor may be ascertained from the specific gravity, allowance being made for the fact that each 1% of camphor present increases the specific gravity by 0·00116.

W. P. S.

**Estimation of Cyanogen.** HIDEKICHI YANAGISAWA (*J. Pharm. Soc. Japan*, 1922, 369—377).—The method is based on

the conversion of cyanogen into ammonia. A cyanogen compound is heated with dilute sulphuric acid in a sealed tube at 200° during four hours; after cooling, the product is transferred to a Kjeldahl flask, and after making alkaline with sodium hydroxide, the ammonia is distilled into *N*/4-sulphuric acid; the excess is titrated with *N*/4-ammonia as usual. K. K.

**Comparison of Methods for the Estimation of Urea.** J. CARRA (*Biochim. terapia sper.*, 1921, **8**, 225).—A comparison of various methods for the estimation of urea shows that a gravimetric method based on the formation of a compound of 1 mol. of carbamide and 2 mols. of xanthydrol is extremely exact. The urease method is also excellent. CHEMICAL ABSTRACTS.

**Influence of Sodium Fluoride on the Estimation of Urea by the Xanthydrol Method.** M. POLONOVSKI and C. AUGUSTE (*Compt. rend. Soc. Biol.*, 1922, **86**, 1027—1028; from *Physiol. Abstr.*, 1922, **7**, 214).—The presence of sodium fluoride renders the results obtained by this method too high. This is probably due to the liberation by the acetic acid of hydrofluoric acid. The error may be avoided by the removal of the fluoride by calcium acetate. W. O. K.

**Microchemical Detection of Tryptophan in the Plant.** FRITZ KRETZ (*Biochem. Z.*, 1922, **130**, 86—98).—Tryptophan can be detected in plant-tissues by Fürth's modification of Voisenet's reaction, if the tissues be preserved in a silica gel by soaking in sodium silicate and subsequent addition of concentrated hydrochloric acid. Tryptophan is found in moulds and richly in the embryonic tissues of higher plants and in all other parts containing protein. H. K.

**Uric Acid. I. Examination of the Variables in the Folin and Wu Uric Acid Method. II. A Modification of the Folin and Wu Uric Acid Method.** GEORGE W. PUCHER (*J. Biol. Chem.*, 1922, **52**, 317—327, 329—334).—Using Folin and Wu's method (A., 1919, ii, 308) for the estimation of uric acid in blood, only 75% of added uric acid was recovered. When, however, the solution was heated before filtering the coagulated proteins, a recovery of 93% was obtained. E. S.

**Rapid Estimation of Uric Acid in Urine.** E. VAILLANT (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 178—180).—The liquid is titrated with a standard iodine solution made by dissolving 3·78 grams of re-sublimed iodine and 15 grams of potassium iodide in a little water and diluting to 1 litre. Two c.c. of this solution oxidise 0·005 gram of uric acid (to alloxan and urea). The analysis is carried out by measuring into a small tube 2 c.c. of iodine solution and 1 c.c. of carbon disulphide and allowing the urine to fall a drop at a time from a burette, shaking the tube after each addition, until the carbon disulphide becomes first pale rose and then colourless. The uric acid content per litre of urine is then calculated by dividing the number of c.c. used into 5. Sugar and small amounts of albumin do not interfere; larger amounts of albumin should be

removed by heating to coagulate and then filtering. If the urine is alkaline, a few drops of acetic acid are added; if it contains crystals of uric acid, it is warmed until they dissolve and the analysis is conducted at 25—30°. A. R. P.

**Direct Estimation of Uric Acid in Urine.** STANLEY R. BENEDICT and ELIZABETH FRANKE (*J. Biol. Chem.*, 1922, **52**, 387—391).—The same reagents are employed as in the method for blood (this vol., ii, 405). To 10 c.c. of the diluted urine (containing 0·15 to 0·30 mg. of uric acid) are added 5 c.c. of the sodium cyanide solution and 1 c.c. of the arsenophosphotungstic acid reagent. After five minutes, the mixture is diluted to 50 c.c. and the colour compared with a standard containing 0·2 mg. of uric acid similarly diluted to 50 c.c. Owing to the larger amount of uric acid present in urine than in blood, it is unnecessary to heat the solution. Of the other constituents of urine, albumin appears to be the only one which interferes with the reaction. This may be removed, if present, by coagulation by heat in the presence of a drop of acetic acid. E. S.

**Rapid Estimation of Quinine Salts.** S. G. LIVERSEDGE and F. W. ANDREWS (*Pharm. J.*, 1922, **109**, 92—94).—Quinine in quinine salts is rapidly estimated by dissolving the alkaloidal salt in 20 c.c. of $N/5$-sulphuric acid, a known excess of $N/2$-sodium hydroxide is then added and the liberated quinine extracted with ether saturated with water, and subsequently the excess of alkali titrated with $N/5$-sulphuric acid, using phenolphthalein as indicator. The amount of acid originally combined with quinine is thus determined, whence the percentage of quinine or quinine salt is obtained by calculation. If boric acid is present, hæmatoxylin is used as indicator. G. F. M.

**Estimation of Small Quantities of Atropine in Blood-serum.** H. C. VAN DER HEYDE (*J. Lab. Clin. Med.*, 1922, **7**, 280—287).—Atropine was estimated in 1 c.c. of serum in maximum concentrations of 0·5%. Proteins are first precipitated with absolute alcohol, the precipitate being washed several times with absolute alcohol, and the alcoholic filtrates evaporated to dryness. The residue is treated with a small quantity of water and the solution filtered from fats on a microfilter. The dilution is then determined in which Mayer's reagent (potassium mercury iodide) will just give a precipitate, and compared with control solutions of known dilution. CHEMICAL ABSTRACTS.

**Method for the Separation of Strychnine from Quinine.** NORMAN EVERS (*Pharm. J.*, 1922, **109**, 90—91).—A practically quantitative separation of strychnine from quinine is achieved by taking advantage of the fact that chloroform extracts strychnine hydrochloride from strongly acid aqueous solutions, but does not remove quinine hydrochloride under similar conditions. The solution of the mixed alkaloids is acidified with hydrochloric acid to make it about $2N$, and is extracted with five successive quantities of 50 c.c. each of chloroform. The chloroform extracts are united,

concentrated to 50 c.c., shaken with dilute aqueous ammonia, and evaporated to dryness. The residue is almost pure strychnine, and the quinine is extracted from the residual acid solution with chloroform after rendering alkaline in the usual way. G. F. M.

**Detection of Thymine in the Presence of Sugar.** HARRY J. DEUEL and OSKAR BAUDISCH (*J. Amer. Chem. Soc.*, 1922, **44**, 1581—1584).—A modification of the method, described recently by Johnson and Baudisch (this vol., ii, 238) for the detection of thymine, is given which makes it applicable in the presence of sugar. For this purpose, the thymine is precipitated as the mercury salt by the addition of saturated mercuric chloride solution (10 c.c.) and sufficient sodium hydroxide solution to make the mixture distinctly alkaline. The precipitate is separated by means of a centrifuge, and, after pouring off the supernatant liquid, it is thoroughly mixed with about 100 c.c. of distilled water and again centrifuged. It is then suspended in water (100 c.c.) and decomposed with hydrogen sulphide; the precipitated mercuric sulphide is filtered and excess of hydrogen sulphide is removed by boiling the filtrate. The remaining liquid is cooled and made up to 100 c.c. Oxidation of the thymine is effected by treating the solution with sodium hydrogen carbonate and ferrous sulphate in the presence of air and the test is completed as described previously. Thymine in quantities of 10—15 mg. may readily be detected in the daylight, whilst as small a quantity as 1 mg. may be detected by the use of the iron arc light. H. W.

**Recognition of Proteins and Derivatives by Colour Reactions.** M. A. RAKUSIN (*Biochem. Z.*, 1922, **130**, 268—281).—The author has examined a large number of animal and vegetable proteins, ferments, and toxins in respect of their behaviour towards eight colour reagents, namely, biuret, Millon's, xanthoprotein, Liebermann's, Adamkewitsch's, Molisch's, Pettenkofer's, and Ostromysslenski's, and the behaviour towards the sulphur reaction of Vohl and Rakusin. Each protein corresponds with a definite complex of reactions. H. K.

**Estimation of Small Amounts of Albumin in Urine.** G. GÉRARD (*Bull. sci. pharmacol.*, 1921, **28**, 466—467; from *Physiol. Abstr.*, 1922, **7**, 158—159).—Ten c.c. of urine are placed in each of two test-tubes. One is warmed and a few drops of trichloroacetic acid are added, giving the usual turbidity when albumin is present. To the other there is added drop by drop officinal spirit of peppermint. The tube and contents are shaken after each drop is added, and the turbidity of the two tubes is compared. When the opacity of both is alike, the test is completed. The author has found that 1 drop of the alcohol used is equivalent to 0·04 c.c. of albumin. No results are given. W. O. K.

**The Differential Precipitation of the Proteins of Colos-**
The **um and a Method for the Estimation of the Proteins in**
the n**strum.** PAUL E. HOWE (*J. Biol. Chem.*, 1922, **52**, 51—68).—
pubumin cow's colostrum is precipitated by addition of successive
iantities of sodium sulphate, a precipitation curve is

obtained which shows three "critical zones" at which increases in the concentration of sodium sulphate cause only small increases in the amount of protein precipitated. These zones occur at concentrations of 13·5—14·5, 17·4—18·4, and 21—22% of sodium sulphate. Up to concentrations of 13·5% euglobulin is precipitated, between 14·5 and 17·4% a mixture of caseinogen and ψ-globulin I is obtained, whilst the precipitate produced between 18·4 and 21% is termed ψ-globulin II. After removal of euglobulin, caseinogen may be precipitated separately by addition of either acetic acid or alum. Total precipitation, including albumin, is effected by means of trichloroacetic acid. By combining these precipitations with Kjeldahl estimations on the filtrate before and after precipitation, a method for the estimation of the proteins of colostrum and of milk is developed (cf. Woodman, A., 1921, i, 625).

E. S.

**Estimation of Globulins in Blood-serum.** R. R. HENLEY (*J. Biol. Chem.*, 1922, **52**, 367—375).—Two methods are described. In the first, the globulins are precipitated by saturation with magnesium sulphate and the non-globulin nitrogen is estimated in the filtrate. The difference between this and the total nitrogen gives the globulin nitrogen. In the second method, the globulins are precipitated by half saturation with ammonium sulphate, filtered, dissolved in salt solution, and again precipitated. The precipitate is once more dissolved in salt solution and the globulins are finally precipitated by boiling, one or two drops of 10% acetic acid being added if necessary. The precipitate is then filtered on to a tared, hardened filter-paper, washed, dried at 100°, and weighed. The results obtained by both methods vary slightly according to the dilution employed, but are otherwise in agreement with those obtained by Cullen and Van Slyke's method (A., 1920, ii, 398).

E. S.

**New Method for the Detection of Bile Pigments.** AL. IONESCU and C. POP (*Bul. Soc. Chim. Romania*, 1922, **4**, 20—26).—The following method is recommended as a quick and satisfactory means of detecting bile pigments in urine. To 10 c.c. of the urine are added 2 c.c. of a 0·5% solution of albumin and a few drops of 10% acetic acid. The mixture is boiled and filtered. The precipitate is washed with water and to it on the filter-paper is added one drop of a mixture of 4 c.c. of 6% potassium dichromate and 1 c.c. of 20% sulphuric acid. If the urine contains bile pigments the yellow precipitate turns a green or bluish-green colour. The depth of the colour depends on the amount of pigment present. The reaction is characteristic and very sensitive and is not given by other normal or abnormal urinary pigments. W. G.

**Estimation of Bilirubin in Human Serum. The Ehrlich-Pröscher Reaction.** J. S. THANNHAUSER and E. ANDERSEN (*Deut. Arch. klin. Med.*, 1921, **137**, 179—186; from *Chem. Zentr.*, 1922, ii, 425).—The colorimetric method of Hijmans van den Bergh, in which, after precipitation of protein from serum by means of ethyl alcohol, bilirubin is directly combined with diazobenzene-

sulphonic acid, is considered to be inexact owing to precipitation of a portion of the bilirubin by ethyl alcohol and also owing to the coloration obtained differing from that of the test solution. The latter difficulty can be avoided by the presence of excess of mineral acid. Directions are given for the estimation of bilirubin in different sera. G. W. R.

**Estimation of Trypsin. A Modification of Gross's Method.** Sotaro Kai (*J. Biol. Chem.*, 1922, **52**, 133—136).—The relative strengths of trypsin are estimated by measuring the time taken by equal amounts of each to digest 25 c.c. of a casein solution, the time of digestion being inversely proportional to the concentration of trypsin. The end-point of digestion is determined by adding a sodium hydroxide–acetic acid solution to test portions withdrawn from time to time, no precipitate being produced when digestion is complete. By arbitrarily choosing one preparation as standard, the concentrations of others may be expressed in terms of this. E. S.

**Acidosis. XVIII. Estimation of the Hydrogen Carbonate Concentration of the Blood and Plasma.** Donald D. Van Slyke (*J. Biol. Chem.*, 1922, **52**, 495—499).—Two methods are described. In the first, total carbon dioxide is estimated by Van Slyke and Stadie's method (this vol., ii, 78) and $P_H$ either electrometrically or colorimetrically by Cullen's method (following abstract). The hydrogen carbonate concentration is then calculated from the equation $[BHCO_3]=[CO_2]/(1+10^{P_{K_1}-P_H})$, which is derived from $[H^{\cdot}]=K'.[H_2CO_3]/[BHCO_3]$, $P_{K'}$ being the negative logarithm of $K'$. The second is a titration method. One c.c. of plasma is treated with 5 c.c. of 0·01*N*-hydrochloric acid and shaken in a 100 c.c. round flask to remove carbon dioxide. It is then brought back to the original alkalinity by the addition of 0·01*N*-sodium hydroxide, phenol-red being used as indicator and 1 c.c. of the original plasma as standard. Sodium chloride solution (0·9%) is used for the preparation of the standard acid and alkali, and also for the dilution, where necessary, of the plasma. Special precautions must be observed to prevent loss of carbon dioxide from the standard. E. S.

**Acidosis. XIX. Colorimetric Estimation of the Hydrogen-ion Concentration of Blood Plasma.** Glenn E. Cullen (*J. Biol. Chem.*, 1922, **52**, 501—515).—The hydrogen-ion concentration of diluted plasma or serum is estimated colorimetrically at 20° by comparison with Sörensen's phosphate standards, using phenol-red as indicator, and is then converted into that for undiluted plasma at 38° by use of an empirical factor. The latter has been determined by direct comparison of colorimetric with electrometric estimations, and has been found to be constant for plasma of the same species. It is different, however, for plasma of different species and also for plasma and serum of the same species. The success of the method depends on the use of a technique, which is described in the original, to prevent the loss the carbon dioxide during both the preparation of the plasma and pibumstimation. E. S.

# General and Physical Chemistry.

**The Reflexion of X-Rays by Crystals.** R. Dardord (*J. Phys. Radium*, 1922, [vi], **3**, 218—220).—When $X$-rays are reflected from a cylindrical crystalline surface, such as may be obtained by bending a sheet of mica, the analogy between the reflexion of $X$-rays and light becomes closer; the only difference is that the reflexion of the former is selective. An image of a rectilinear source of $X$-rays may be obtained from a cylindrical surface and received on a photographic plate. The theory of the formation of the image is discussed and this verified experimentally. W. E. G.

**Errors arising in the Measurement of Unsymmetrical Spectrum Lines.** T. R. Merton and D. N. Harrison (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 431—434).—One of the most serious sources of error in the measurement of the spectrum lines by juxtaposition of an arc spectrum is the drift of the spectrum across the plate due to either mechanical displacement or changes in the temperature of prism or grating. The methods frequently employed to reduce these errors are not satisfactory for unsymmetrical lines. It is shown that the position of the maximum of an unsymmetrical line in the case of a uniform drift lies at the intersection of the intensity distribution curves at the beginning and the end of the exposure, and hence in the comparison with symmetrical lines, errors amounting to a large fraction of the displacement may easily occur. For this reason, the spectra of gases at low pressures, in which the lines are known to be symmetrical, are to be preferred as standards of wave-length. W. E. G.

**Atomic Hydrogen and the Balmer Series Spectrum.** R. W. Wood (*Phil. Mag.*, 1922, [vi], **44**, 538—546).—From the investigation of the hydrogen spectrum developed by an electric discharge in long vacuum tubes containing hydrogen (A., 1921, ii, 665), it is concluded that the secondary spectrum is emitted by the hydrogen molecules, the Balmer series by the atoms. The latter series has been extended to the 20th line by abolishing the secondary spectrum and the faint continuous background of illumination and employing a sufficiently long exposure. It appears extremely probable that the part played by water vapour in enhancing the development of the Balmer series consists in supplying a "poison" (oxygen) to the catalysing wall of the discharge tube, thus permitting a high concentration of atomic hydrogen in the tube under the action of a heavy discharge. With a feeble discharge, the secondary spectrum predominates, as atomic hydrogen is not formed sufficiently fast to overtake the catalysing power of the tube wall. The whiteness of the discharge when the discharge tube is immersed in liquid air, observed by Merton, is due to the increased catalysing power of the wall at low temperatures. The catalysis theory is

likewise applicable to explain the characteristic spectrum developed when air or nitrogen is admitted to the discharge tube containing hydrogen, and the more complete development of the Balmer series in the solar corona and probably in nebulæ. The wave-lengths of the components of the doublet $H_\gamma$ were found to be 4340·494 and 4340·435 I.Å. J. S. G. T.

**The Emission Spectrum of Monatomic Iodine Vapour.** St. Landau-Ziemecki (*Phil. Mag.*, 1922, [vi], **44**, 651—656).—The band spectrum of iodine vapour at low temperatures showed distinct maxima at λλ 422, 404, 395, 387, 380, 373, 368, 363, 340, 325, 323, 320, 319, 312, 310, 306, 304, 302, and 299 μμ. The band spectrum became gradually fainter and the line spectrum developed as the temperature was raised. At 960—1000°, corresponding with almost complete dissociation of the iodine molecules, the band spectrum disappeared entirely and was replaced by the line spectrum, due to atomic iodine vapour, and consisting of wave-lengths 4868, 4769, 4680, 4324, 4132, 4100, 3384, 3281, 3081, 2879, 2593, 2583, and 2566 Å. Of these, λ 3281 Å. is certainly new. It is concluded that the band spectrum originates in the molecule, and the line spectrum in the atom. J. S. G. T.

**The Spectrum of Helium in the Extreme Ultra-violet.** Theodore Lyman (*Nature*, 1922, **110**, 278—279; cf. Fricke and Lyman, A., 1921, ii, 362).—When an improved apparatus is used, the line at 584·4 is of very great strength, and is accompanied by three new lines at 537·1, 522·3, and 515·7, of which the intensities decrease with the wave-length in a manner strongly suggesting a series relation. The spacing of these lines on the frequency scale is identical with that of the first four lines in the singlet principal series. The line at 584 is therefore regarded as the first member of a principal series, *oS—mP*. The wave-lengths of the new lines, however, are not in complete agreement with the accepted values of the resonance and ionisation potentials. A. A. E.

**Some Spectrum Lines of Neutral Helium derived theoretically.** Ludwik Silberstein (*Nature*, 1922, **110**, 247—248).—Owing to the prohibitive nature of the general problem of three or more bodies, Bohr's quantum theory can account only for those spectrum lines which form a series of the simple Balmerian type, that is (apart from *X*-ray spectra of the higher atoms), only those of atomic hydrogen and ionised helium. An attempt is therefore made to obtain a special solution to the problem in the case of neutral helium, the spectrum of which, containing some 105 lines, has not been accounted for theoretically. Assumption that the nucleus and the two electrons are always collinear with each other, the latter describing two equal and oppositely situated ellipses round the former, is evidently erroneous, since the corresponding formula does not cover a single observed line of helium. On the other hand, assumption that the mutual perturbation of the two electrons is negligible yields a spectrum formula which covers about forty lines of the spectrum of neutral helium, and will

probably be found to cover fifty more lines. It therefore appears that the electrons within the atom do not repel each other even with a small fraction of the force usually attributed to them. Lithium appears to yield similar, although less striking results. It is concluded that the field of force of a bound electron is entirely engaged by the nucleus, at least in the case of helium and probably lithium, but possibly also in that of the higher atoms. A. A. E.

**Spectrum Lines of Neutral Helium.** W. M. HICKS (*Nature*, 1922, **110**, 309).—The constitution of the secondary spectrum of hydrogen may be examined by a method similar to that used by Silberstein (preceding abstract) for helium. Practically the whole of this spectrum depends on the sequence of the Balmer series. If $f(m)$ denote the $m$th sequent, the wave-length of any line is of the form $\Sigma k_m f(m)$, where the $k_m$ are positive or negative integers. The spectrum is a kind of linkage spectrum in which the usual links are replaced by the separations between the successive lines of the primary, namely, 5331·57, 2467·75, etc. In Silberstein's theory, as in all orbital theories, the two electrons are considered to be moving independently, and each to pass between two of its corresponding paths; if, however, the combined change of energy is radiated, these two events must be simultaneous. A. A. E.

**Ionisation in the Solar Atmosphere.** HENRY NORRIS RUSSELL (*Astrophys. J.*, 1922, **55**, 354—359).—Barium is much more highly ionised in the sun than sodium, although their ionisation potentials are the same. The absorption of photospheric radiation by atoms in the solar atmosphere tends to increase the degree of ionisation, both directly, by shifting an electron into a position from which its removal is easier, and indirectly, when enhanced lines are absorbed, by getting the ionised atoms into states in which they are probably less likely to combine with electrons. The case of lithium, however, is anomalous. Barium lines and enhanced rubidium lines in the solar spectrum are tabulated. The ionisation potential of manganese (7·6 volts) agrees well with the value predicted from the behaviour of its lines in the solar spectrum. A. A. E.

**The Spectrum of Glucinum and its Noteworthy Relation to the Spectrum of Aluminium.** L. C. GLASER (*Ann. Physik*, 1922, [iv], **68**, 73—88).—Employing the arc or spark between electrodes of glucinum, the author has investigated the spectrum of the metal in the visible and ultra-violet regions. The line spectrum observed confirms, with certain limitations, the previous measurements of Rowland and Tatrall. In the region λλ 5500—1900 Å., no lines, apart from those constituting part of the band spectrum, attributable with certainty to glucinum, were observed. The line spectrum observed was constituted of λλ 4607 ?, 4600 ?, 4572, 4486·7 ?, 4277·8 ?, 4263·6 ?, 4216·0, 4079·0, 3994·0, 3936·0, 3909·3, 3891·0. A more accurate measurement of the strongest line, λ 4572, gave the result 4572·73±0·0098 Å., in terms of the normal international iron spectrum. Attention is directed to

certain analogous physical features characterising the production of the band spectra of glucinum and aluminium. The wave-lengths of the constituent bands in the spectra of both elements are tabulated, and it is remarked that there is considerable agreement between the respective first differences of wave-lengths of successive lines in corresponding bands in the two spectra. Deslandre's rule is true only as a first approximation. Attention is also directed to the approximate constancy of certain numerical values calculated from the wave numbers of the heads of the bands λλ 4708 and 4842 in the case of the glucinum and aluminium spectrum, respectively. It is concluded that the atomic structures of glucinum and aluminium, so far as the emission of their band spectra is concerned, are the same. J. S. G. T.

**The Band Spectra of Cadmium.** Erik Hulthén and Ernst Bengtsson (*Compt. rend.*, 1922, **175**, 423—426).—Two systems of bands have been measured at λ=4500 and λ=4300 and their structures studied. The results show that the bands of the elements zinc, cadmium, and mercury can be embodied in the same expressions, and the constants of the series in the bands of cadmium are given. W. G.

**A Continuous Spectrum from Mercury Vapour.** C. D. Child (*Astrophys. J.*, 1922, **55**, 329—344; cf. A., 1921, ii, 3).—A continuous spectrum identical with the fluorescence spectrum is emitted in addition to the ordinary line spectrum when (*a*) the temperature of the vapour is above 120° and below 300—400°, depending on the pressure, (*b*) the pressure is above 1 mm., (*c*) the current density is low, (*d*) very little air or other contaminating gas is present. Ionisation of the vapour is not, however, necessary. It is suggested that the carriers of the spectrum are molecules consisting of two or more atoms, which emit the fluorescence spectrum as a result of excitation by ultra-violet radiation λ 2536 emitted by atoms struck by electrons with energies corresponding with at least 4·9 volts. The ionisation potential for mercury appears to vary with the temperature, reaching a minimum at about 140°. Above 120°, mercury vapour reacts with air to form a dark compound; the reaction is associated with the appearance of the continuous spectrum. A continuous spectrum of sodium, much fainter than the line spectrum, has also been observed.

A. A. E.

**The Lanthanum Violet Bands and the Associated Lines.** Junzô Ôkubo (*Sci. Rep. Tohoku Imp. Univ.*, 1922, **11**, 95—104).—The edges of the bands in the violet and green regions of the lanthanum spectrum consist of closed doublets, and the edges of these are determined accurately in order to seek a relation between the band and line spectra. The best conditions for observing the bands and diffused lines are obtained when the temperature of the arc is low, or by using lanthanum as the negative electrode with a moderate current; under these conditions, the sharp lines are comparatively faint. It was found that one pair of double

lines exists nearly midway between the corresponding heads of each series of bands, and another between the heads of successive series so that the bands are not independent of each other. By the introduction of the quantum theory, the conclusion is drawn than the lanthanum violet bands are emitted as a consequence of the molecular rotation when line emission takes place in the atom, thus accounting for the double structure of the bands.

W. E. G.

**The Arc Spectra of Gallium and Indium.** H. S. Uhler and J. W. Tanch (*Astrophys. J.*, 1922, **55**, 291—301).—By the use of a concave grating with 590 lines per mm. and a radius of curvature of 640 cm., accurate determinations were made of the wave-lengths for air and the vacuum wave numbers of twenty-three gallium lines and thirty-four indium lines, λ 4511 to λ 2170. All the gallium lines and twenty-eight of the indium lines were found to belong to the two subordinate series, for each of which from five to eight terms were identified. Four indium lines, previously supposed to be single, were resolved. An attempt to obtain the absorption spectrum of indium vapour gave only the two strongest lines, λ 4511 and λ 4102. A. A. E.

**Optical Experiment Demonstrating the Bragg Method of Crystal Analysis.** Bilfried Quarder (*Physikal. Z.*, 1922, **23**, 350—352).—An optical analogue to the distribution of intensities in the various orders of *X*-ray spectra reflected from the 1, 1, 1, planes of sodium chloride or the 1, 0, 0 planes of zinc sulphide is afforded by the use of a photographic grating consisting of equally spaced, alternately thick and thin lines. By reducing the grating aperture, broadening of the lines occurs, a result analogous to the broadening of the lines in the *X*-ray spectrum, occurring on powdering the diffracting crystals, as observed by Debye and Scherrer (A., 1917, ii, 437). J. S. G. T.

**Spectra of X-Rays and the Theory of Atomic Structure. IV and V.** D. Coster (*Phil. Mag.*, 1922, [vi], **44**, 546—573).—In continuation of previous work (A., 1922, ii, 491), the author has investigated the *L*-series of the characteristic *X*-ray spectra of the rare elements from lanthanum (atomic number 57) to lutecium (atomic number 71). In general, the lines for these elements are much sharper than those for elements of lower atomic number, and most of the stronger lines are accompanied by fairly intense satellites. Measurements have been made of a great number of lines which may be arranged in a simple diagram and are conveniently referred to as diagram lines, a number of non-diagram lines, and some absorption discontinuities. The measured frequencies of the diagram lines are in agreement with results to be anticipated from Bohr's theory of the successive development of the shells of electrons in the various atoms. Most of the non-diagram lines lie on the short wave-length side of an intense diagram line, and the difference of frequency between the two lines is approximately proportional to the atomic number of the element.

A theoretical discussion is given of the origin of the non-diagram lines and of the fine structure of the absorption discontinuities. In criticism of the views of Wentzel (this vol., ii, 249) in this connexion, experimental results have been obtained showing that the assumption of the successive ionisation of the inner shells of the atom is untenable, and that part of the non-diagram lines are emitted by atoms which have lost more than one electron at the same time by the impact of a single high-speed β-particle. An explanation is given of the origin of some non-diagram lines lying on the long wave-length side of diagram lines, and it is suggested that these lines should appear both in the emission and in the absorption spectra. J. S. G. T.

**Analysis of the Electronic Structure of the Elements.** A. DAUVILLIER (*J. Phys. Radium*, 1922, [vi], **3**, 221—251).—The author has investigated the *L*-series of lines in the characteristic *X*-ray spectra of uranium, gold, platinum, iridium, osmium, tungsten, and antimony, and the *K*-lines in the spectra of copper and molybdenum (cf. A., 1921, ii, 669; this vol., ii, 43, 101, 559). The numbers of observed lines have been at least doubled, and owing to the correction of certain errors, it is shown that Sommerfeld's theory is applicable to the calculation of the frequencies of these lines. The results have been applied to determine the energy levels of the atoms of most of the elements and afford a complete qualitative explanation of their absorption spectra; they have likewise been correlated with the ionisation potentials of certain gases and metallic vapours, by the application of the quantum hypothesis. The numbers of electrons in the various corpuscular layers of the respective elements have been calculated, and it is shown that the number $n$ of such electrons is related to the quantum number $\tau$ characterising the layer by the equation $n=2\tau^2$. A theory is advanced to account for the complex structures of the *K* and *L* series of lines in the *X*-ray spectra of the light elements, and these spectra are, by the aid of the theory, correlated with the corresponding spectra of the elements in the visible region. The variation of atomic volume and chemical valency of the elements, as shown by the periodic table, is also at least partly explained by the theory developed. J. S. G. T.

**The Absorption Spectrum of Potassium Vapour.** SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 539—547).—The principal series lines in the absorption spectrum of potassium vapour have been measured up to $m=42$ (compared with $m=24$ previously). Satisfactory agreement is shown between the measured frequencies and those calculated by the series formula $p_1(m)=35008{\cdot}480-109736{\cdot}1/(m+1{\cdot}29667-0{\cdot}06154/m)^2$, except for $m=3$ and $m=39$ to 42. The value for $m=3$ is abnormal, and the latter values receive a possible explanation along the lines of Sommerfeld's assumption of the occurrence of collisions between the electrons emitted from the atom and other electrons or atoms. The first seven members of the principal series have been resolved, compared with five previously. New absorption lines, first

appearing at 20 mm. pressure, and apparently not corresponding with known lines in the emission spectrum, were found at higher pressures. The combination lines $1s$—$2d$ and $1s$—$3d$ were found to be absorbed, the first as a pair, confirming the presence of a satellite to the lines of the diffuse series. The appearance of these absorption lines contradicts the selection principle. J. S. G. T.

**Absorption of Potassium Vapour in the Associated Series.** A. L. NARAYANA and D. GUNNAIYA (*Nature*, 1922, **110**, 250).—Traces of absorption occur at about 1100°. In the diffuse series, distinct traces of absorption have been detected; the bands 5780, 5340, 5300, and 5100 apparently correspond with 5782, 5340, 5323, and 5100 of ($2p$—$m.d$). A. A. E.

**Absorption of Light by Sodium and Potassium Vapours.** GEORGE R. HARRISON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 260—263).—Vapour density alone determines the development of the continuous absorption spectrum of sodium vapour. No visible effect is attributable to hydrogen present in pressures up to 400 mm. of mercury. Absorption begins at the last resolved line of the principal series. No definite break in the continuous absorption spectrum was observed, but the absorption decreases rapidly with decreasing wave-length, the region λ 2200 Å. being one of the most transparent regions studied. With unsaturated sodium vapour, the band spectrum is much weaker than the line and continuous spectra. It is suggested that the bands are due to loose molecular aggregates. Fluorescence, which was marked in saturated vapour, disappeared on superheating the vapour. The continuous absorption spectrum of potassium vapour resembled that of sodium. J. S. G. T.

**The Absorption and Fluorescence Spectra of Benzene.** VICTOR HENRI (*J. Phys. Radium*, 1922, [vi], **3**, 181—211).—The ultra-violet spectrum of benzene has been studied over pressures ranging from 0·01 to 65 mm. At the low pressures the absorption bands are resolved into a series of narrow bands, about 0·15 Å. apart, which fuse very readily on passing a certain limited pressure. They are distributed in eight groups, of which only five are visible at 0·01 mm. More than 350 bands have been counted.

The application of Bohr's theory to the study of these band spectra permits of their classification into four series, each band being given by an equation of the form $1/\lambda = A - B + na - (pb + p^2b') + \alpha(m^2 - q^2)$, in which $A$, $B$, $a$, $b$, $b'$, and $\alpha$ are constants and $n$, $p$, $m$, and $q$ whole numbers. The intensities of the heads of the bands are greatest for $p=0$ and diminish rapidly as $p$ increases, which is in agreement with the theory. The coefficients deduced from the results of the ultra-violet absorption are available for the calculation of the infra-red absorption spectra of benzene. The terms $A$ and $B$ are due to electronic movements and do not enter into the frequency of the infra-red absorption bands, for which a simple formula is deduced, $1/\lambda = an - bp$; the agreement between the calculated and experimental values is very satisfactory. The moment of inertia of the benzene molecule ($I = 1{\cdot}45 \times 10^{-38}$) is

derived from the value of the constant $a$ and compared with that calculable from the crystal models of benzene derivatives deduced by Bragg.

The ultra-violet spectra of liquid benzene and its solutions correspond closely with the spectra of the vapour, except for a slight shift towards longer wave-lengths. On dilution, the specific effect of the solvent becomes more marked, the bands widen and move towards the red; this effect, which is analogous to the Stark effect, may be due to the action of an intense electric field of the solvent molecules. The displacement does not bear any relation to the dielectric constant of the solvent. The fluorescent spectrum of liquid benzene consists of six bands, which are excited by monochromatic light of wave-lengths lying within the benzene absorption bands *D*, *E*, *F*, *G*, and *H*; lines which correspond with the *A* and *B* absorption bands do not excite any fluorescence. The molecules absorbing the monochromatic light do not return to their original state on the emission of the fluorescent light, and the fluorescent bands lie towards the red with respect to the absorption bands. When the vapour of benzene is subjected to a high frequency discharge, a new absorption band appears ($\lambda$=2750·5 Å.).

W. E. G.

**The Ultra-violet Absorption Spectra of Dihydric Phenols.** F. W. Klingstedt (*Compt. rend.*, 1922, **175**, 365—367).—The quantitative study of the absorption spectra of dihydric phenols in hexane solution has given new results. Diagrams of the normal spectra of phenol, resorcinol, catechol, and quinol are given. These show that *m*- and *o*-derivatives yield results similar to those obtained with phenol, whilst the *p*-compound possesses a series of eight distinct bands in place of three exhibited by the other substances. This is a general result, as shown by the spectra of other benzene derivatives. The spectra are considerably modified by the solvents used, especially by alcohol; the authors consider that, as alcohol has been used for much work on absorption spectra, the observations should be repeated with hexane solutions. H. J. E.

**Phosphorescent Zinc Sulphide containing Copper.** B. Gudden and R. Pohl (*Ann. Physik*, 1922, [iv], **68**, 154—156).—Wilde has recently investigated the variation of the dielectric constant of phosphorescent zinc sulphide containing copper due to illumination, a phenomenon previously studied by the authors and by Molthan. Briefly, the results indicate that the increase in the value of the dielectric constant due to illumination is a maximum at about 140°. The effect is small at high temperatures. Temporary fluctuations of the effect at all temperatures, and for all exciting wavelengths, is correlated with the luminosity of the phosphorescent substance. Regarding the phenomenon as originating in certain centres of excitation surrounding the relatively few copper atoms present, it follows that the effect must decrease with increasing temperature, and increase to a limiting value with decrease of temperature. The occurrence of the experimentally determined maximum at 140° is explained by assuming that the mobility of the electrons

within the excited centres diminishes as the temperature is reduced, an assumption which is in accord with other experimental results. The failure to detect the effect in other varieties of these phosphorescent substances is regarded as a matter of accuracy of measurement. J. S. G. T.

**Fluorescence, Photochemical Action, and Einstein's Law.** FRITZ WEIGERT (*Z. Physik*, 1922, **10**, 349—351).—A theoretical paper in which the author criticises Perrin's theory of fluorescence (cf. A., 1918, ii, 418; 1919, ii, 177). The part played by oxygen in the photochemical change of most fluorescent substances demonstrates the independence of the fluorescence and the sensitivity to light. For example, an oxygen-free solution of fluorescein is stable to light. The photochemical reaction velocity decreases with increasing partial pressure of oxygen, whereas the brightness of the fluorescence is unaffected. The experiments of Wood and Pringsheim are to be explained along these lines. Einstein's law cannot be applied to these photochemical processes, since under the most favourable conditions 200 energy quanta are necessary for the absorption of one molecule of oxygen by the fluorescent substance. W. E. G.

**Ionisation of Potassium Vapour by Light.** R. C. WILLIAMSON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 255—260).—By employing a jet of hot potassium vapour, directed into a cool vacuum chamber and traversed by a pencil of light derived from a mercury arc in quartz, evidence has been obtained of the ionisation of potassium vapour by light. The limiting long wave-length (λ 2856 Å.) of the exciting radiation can be calculated from the ionising potential $V$ by the quantum relation $Ve=h\nu$. Below this limit, the ionising power of the radiation increases continuously as the wave-length decreases. J. S. G. T.

**Rise of γ-Ray Activity of Radium Emanation.** F. P. SLATER (*Phil. Mag.*, 1922, [vi], **44**, 300—304; cf. this vol., ii, 13).—Curves are given showing the rise of γ-ray activity from pure radium emanation when enclosed by lead and aluminium of varying thicknesses. The fraction of the ionisation due to radium-$B$ when in radioactive equilibrium with radium-$C$ has been deduced by trial for thicknesses of lead up to 20 mm. The data have been utilised in deducing the absorption coefficients of the heterogeneous γ-radiation from radium-$B$. W. E. G.

**The Distribution of Radioactive Substances in Solutions.** HILARY LACHS and MATHILDE WERTENSTEIN (*Physikal. Z.*, 1922, **23**, 318—322).—In alkaline or neutral solutions of polonium, radium-$D$, radium-$E$, and radium, allowed to remain for a period of hours, the radioactivity exhibited at various depths increases as the depth increases. In acid solutions, the radioactivity is very approximately uniformly distributed throughout the solution. No conclusive results were obtained with solutions of radium-$A$, -$B$, and -$C$. The effects are attributed to the presence of minute particles, derived from the air or the vessel, in the solutions, the

radioactive material being adsorbed by these particles. The results are applied to explain the low values obtained by Paneth for the diffusion coefficient of polonium in neutral and alkaline solution, and of thorium-*B* in alkaline solution. J. S. G. T.

**The Disintegration of Elements by α-Particles.** (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1922, [vi], **44**, 417—432).—The nature of the particles ejected from various elements by bombardment with swiftly moving α-particles (cf. A., 1921, ii, 293), has been investigated by determining the deflexion of the particles in a magnetic field. The results show that the particles ejected from aluminium, phosphorus, and fluorine consist of positively charged hydrogen nuclei. The same is also probably true of boron and sodium. The ranges of the particles ejected, in the forward and backward directions, from nitrogen, aluminium, boron, fluorine, sodium, and phosphorus have been more accurately determined. In all cases, hydrogen particles were ejected in all directions, and the maximum range in the backward direction was less than in the forward direction. The maximum ranges, in cms. of air, of the ejected particles, in the forward and backward directions, respectively, were found to be: boron, 58 and 38; nitrogen, 40 and 18; fluorine, 65 and 48; sodium, 58 and 36; aluminium, 90 and 67; and phosphorus, 65 and 49. Only in the case of nitrogen was the maximum range of the ejected particles in the backward direction much less than that of free hydrogen particles. No particles of range greater than 30 cm. of air, in the forward direction, were ejected from either lithium or glucinum, and there was no evidence of the ejection of long range particles from magnesium, silicon, or chlorine. Of the series of elements from hydrogen to potassium hitherto examined, the active elements (those from which hydrogen nuclei are ejected) are odd-numbered in the order of atomic number in the regular sequence 5, 7, 9, 11, 13, 15. The atomic masses of the active elements are expressed by $4n+a$, where $n$ is a whole number, and $a=3$ for all except nitrogen, for which $a=2$. With the exception of boron, which has two isotopes, the active elements are pure elements. The results indicate that neither lithium nor chlorine has any lightly bound satellites in its nuclear structure. The hydrogen satellite of nitrogen is relatively close to the main nucleus. The nuclei of even light elements are very complex systems, and it is difficult to advance any simple rule to account for the wide difference in structure of successive elements.

J. S. G. T.

**Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropy of Reactions.** ROSCOE H. GERKE (*J. Amer. Chem. Soc.*, 1922, **44**, 1684—1704).—The *E.M.F.* of a number of electrolytic cells has been determined at a number of temperatures and the following values of the *E.M.F.* of the cell at 25° and the temperature coefficient are recorded: Ag|AgCl|HCl($N$)|AgCl|$Cl_2$ (1 atm.), $E=1{\cdot}1362$ volts, $\Delta E/\Delta T=-0{\cdot}00059$ volts/degree; Hg|HgCl|HCl($N$)|$Cl_2$ (1 atm.), $E=1{\cdot}0904$ volt, $\Delta E/\Delta T=-0{\cdot}000945$; Ag|AgCl|KCl($N$)|HgCl|Hg, $E=0{\cdot}045$

$\Delta E/\Delta T=0{\cdot}000338$; Ag|AgCl|HCl($N$)|HgCl|Hg, $E=0{\cdot}0455$, $\Delta E/\Delta T=0{\cdot}000337$; Pb(cryst.)|$Pb(OAc)_2(2N)$|Pb(Hg), $E=0{\cdot}0057$, $\Delta E/\Delta T=0{\cdot}000021$; Pb(stick)|$Pb(OAc)_2$|Pb(Hg), $E=0{\cdot}0057$, $\Delta E/\Delta T=0{\cdot}000015$; Pb(Hg)|$PbCl_2$|HCl($N$)+$PbCl_2$|AgCl|Ag, $E=0{\cdot}4843$, $\Delta E/\Delta T=0{\cdot}000202$; Pb(Hg)|$PbCl_2$|HCl($N$)+$PbCl_2$|HgCl|Hg, $E=0{\cdot}5299$, $\Delta E/\Delta T=0{\cdot}000129$; Tl(stick)|Tl(OH)|Tl(Hg), $E=0{\cdot}0027$, $\Delta E/\Delta T=0{\cdot}000020$; Tl(Hg)|TlCl|NaCl($N$)+HCl($0{\cdot}001N$)TlCl+AgCl|Ag, $E=0{\cdot}7766$, $\Delta E/\Delta T=-0{\cdot}0000794$; Pb(Hg)|$PbI_2$|$Pb(ClO_4)_2(0{\cdot}218M)$+$HClO_4$|$PbI_2$|$I_2$, $E=0{\cdot}8936$, $\Delta E/\Delta T=-0{\cdot}000042$; Pb(Hg)|$PbI_2$|KI($N$)|$PbI_2$+AgI|Ag, $E=0{\cdot}2078$, $\Delta E/\Delta T=-0{\cdot}000189$; and Pb(Hg)|$PbI_2$|KI($0{\cdot}1N$)AgI|Ag, $E=0{\cdot}2135$, $\Delta E/\Delta T=-0{\cdot}000173$. The free energy, $\Delta F_{298}$, the entropy change, $\Delta S_{298}$, and the change of heat content, $\Delta H_{298}$, have been calculated from the *E.M.F.* measurements and the temperature coefficients of a number of reactions. The following are recorded: Ag+HgCl=AgCl+Hg; $\Delta F=-1050$ Cal., $\Delta S=7{\cdot}80$ Cal./degree, $\Delta H=1275$ Cal.; Pb(cryst.)=Pb(Hg), $\Delta F=-263$, $\Delta S=0{\cdot}97$, $\Delta H=26$; Pb(stick)=Pb(Hg), $\Delta F=-263$, $\Delta S=0{\cdot}69$, $\Delta H=-57$; Pb(solid)=Pb(Hg), $\Delta F=-263$, $\Delta S=0{\cdot}74$; $\Delta H=-42{\cdot}4$; Pb(solid)+2AgCl=$PbCl_2$+2Ag, $\Delta F=-22612$, $\Delta S=-8{\cdot}58$, $\Delta H=-25170$; Pb(solid)+2HgCl=$PbCl_2$+2Hg, $\Delta F=-24717$, $\Delta S=6{\cdot}70$, $\Delta H=-22720$; Tl(cryst.)+AgCl=TlCl+Ag, $\Delta F=-17975$, $\Delta S=-1{\cdot}08$, $\Delta H=-18296$; Pb(solid)+$I_2$=$PbI_2$, $\Delta F=-41501$, $\Delta S=-1{\cdot}20$, $\Delta H=-41859$; Pb(solid)+2AgI=$PbI_2$+2Ag, $\Delta F=-9852$, $\Delta S=-7{\cdot}98$, $\Delta H=-12231$; Hg+$\frac{1}{2}Cl_2$=HgCl, $\Delta S=-21{\cdot}80$; and Ag+$\frac{1}{2}Cl_2$=AgCl, $\Delta S=-13{\cdot}73$. The third law of thermodynamics has been submitted to a most rigorous test and discrepancies found earlier by Lewis and Latimer (this vol., ii, 471) have been reduced tenfold. Assuming the validity of the third law, the entropies of chlorine and iodine have been calculated and the following values recorded: $\frac{1}{2}Cl_2$, $S_{298}=27{\cdot}1$; $\frac{1}{2}I_2$, $S_{298}=13{\cdot}5$.
J. F. S.

**Electric Kataphoresis of Metallic Protein Compounds obtained by Treatment with Powdered Metals.** A. Benedicenti and S. Rebello-Alves (*Arch. intern. pharmacodynamie,* 1922, **26**, 297—316).—In shaking a solution of egg-albumin or of blood-serum with powdered metals the metals become attached to the proteins and the properties of the latter change. They become coloured, their reactions are altered, they are not coagulated by heat, and resist putrefaction. The "fixation" of the metals is independent of the reaction of the protein solution and of its gas and salt content. The metals in this combination lose their ionic properties and are not dialysable. Metals vary in their power to combine with proteins: cobalt, copper, and iron combine to a greater extent than do aluminium and lead. Powdered oxides of the metals do not combine with proteins. By passage of an electric current through an alkaline solution of the metallic protein compound, the protein particles become negatively charged and move towards the positive electrode, carrying with them the fixed metal. In an acid solution the protein particles become negatively charged, move to the cathode and a part of the metal is deposited

on the electrode. At the chemically neutral (? isoelectric) poi a protein coagulum forms, which gradually changes into a membra upon which the fixed metal deposits. Boiling or heating a metall protein solution to 50—60° changes profoundly its electrophoret properties. It is suggested that the thermolability of sera, t fixation of metals by certain organs and their elimination, e depend on the formation of metastable protein compounds a on changes in the chemical equilibria of these compounds.

CHEMICAL ABSTRACTS.

**Kataphoresis of Water in Organic Liquids.** A. GYEMA (*Z. physikal. Chem.*, 1922, **104**, 74—88).—The kataphoresis drops of water and aqueous solutions of acids, bases, salts, and d in aniline, guaiacol, and benzonitrile has been measured by microscopic process. In the case of guaiacol (less in aniline a still less in benzonitrile), it is found that water and aque solutions of inorganic electrolytes do not migrate at all or at t only very slowly, whilst solutions of salts which furnish orga ions possess a considerable kataphoric velocity. The sense the direction is exactly that which would be expected from kataphoresis of the same organic liquids in the correspon aqueous solutions. In the case of organic kations, the water d are negatively charged towards the organic medium and organic anions positively charged. Some cases have been fo which point to the assumption that only a portion of the t potential (ε), the so-called ζ-potential, is determinative of kataphoresis. Thus, for example, it is found that drops of aqu solutions of hydrochloric acid and aluminium chloride in be nitrile are positively charged, although when benzonitrile emul in the solutions it is positively charged; this phenomenon its explanation in the ζ-potential. The smaller velocity of migr of drops of aqueous solutions of electrolytes cannot be dir explained by the assumption that in these cases the ζ-pote in the organic liquid is much smaller. Probably it is t explained by the inorganic ions being much less solvated in or liquids than the organic ions. The Helmholtz formula fo velocity of kataphoresis cannot be directly applied to a emulsion in organic liquids.

J. F.

**Thermo-compression and Thermo-addition.** MA DELEUER (*Bull. Assoc. Chim. Sucr.*, 1922, **39**, 477—480 theoretical paper in which the conditions under which the equa moist vapour+moist vapour=superheated vapour, and heated vapour+superheated vapour=moist vapour, are tr discussed.

J. F

**Determination of Specific Heats at Low Tempera** FRANZ SIMON (*Ann. Physik*, 1922, [iv], **68**, 241—280). accuracy of determination of specific heats of substances temperatures devised by Nernst and Schwers (A., 1914, ii been considerably increased by using a larger calor igned so that the amount of liquid hydrogen employed

unnecessarily increased. Determinations have been made and the values tabulated of the respective specific heats of quartz glass, christobalite, "Lindemann" glass, mercury, ammonium chloride, dextrose, cuprous iodide, glycerol, and keton-resin ("Ketonharz," D.R.-P. 309224), at temperatures ranging from 15° Abs. to the ordinary temperature. The $T^3$- law, expressing the value of the molecular heat divided by the number of atoms in the molecule, by the relation $c_p=6{\cdot}94\times10^{-6}T^3$, where $T$ is the absolute temperature, is very closely obeyed by ammonium chloride, for temperatures between 20° and 32° Abs. Anomalous values of the specific heat of ammonium salts are due to a transformation occurring within a certain range of temperature—from about 140° Abs. to 243° Abs. in the case of ammonium chloride. The sudden drop in the value of the atomic heat of glycerol when the temperature is reduced just below 180° Abs. is correlated with the softening of the substance at this temperature. In the case of cuprous iodide, values of the free energy calculated by means of Nernst's theorem are in agreement with experimentally determined values. The values of the energy liberated by the combustion of dextrose at various temperatures are tabulated. The value of $A$, the free energy of the reaction in Nernst's relation, is 704,500 cals. at 290° and 706,700 at 310° $T$. It is shown that the value of the specific heat of complex bodies at different temperatnres can be represented by the Nernst interpolation formula consisting of the sum of the Debye and Einstein functions. The number of the latter functions is small compared with the number of the former. The general characteristics of the variation with temperature of the atomic heats of complex bodies is discussed from the point of view of atomic vibrations, and it is shown why, in many cases, Berthelot's principle affords a close approximation to the energy relations involved. J. S. G. T.

**A New Physico-chemical Law.** HAWKSWORTH COLLINS (*Chem. News*, 1922, **125**, 81—83, 97—98).—From tables of the atomic weight and specific gravity of the elements, and the specific gravity and heat of formation of a number of molecules, the relative volumes of the elements in combination and the heat of formation of the elements when combining to form molecules are deduced. The values calculated never differ more than 1% from the observed values. It is also shown that the heat of formation of each element is proportional to the product of the atomic weight and the change of volume. By change of volume is meant the difference between the volume of the element in the solid state at 15° and the volume of the element in combination with others at 15°. J. F. S.

**Heat of Crystallisation of Quartz.** RAMES CHANDRA RAY (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 509—516).—The heat of crystallisation of quartz has been determined by measuring the respective heats of solution of silver sand and silica glass in hydrofluoric acid. The following values were obtained for the specific heat of aqueous hydrofluoric acid solutions containing the respective percentages by weight of hydrofluoric acid: 10%, 0·908; 20%,

0·838; 30%, 0·756; 34·6%, 0·724. The mean values of the heat of solution in hydrofluoric acid per gram-molecule of silico dioxide were found to be: silica glass, 37·24 Cal.; silver sand 30·29 Cal. The heat of crystallisation of quartz, represented b the difference, is therefore 6·95 Cal. per gram-molecule. Thi value agrees with that calculated from Tschernobaeff and Wolog dine's results, but is much higher than those obtained by Muler (2·21) (A., 1912, ii, 626) and Wietzel (2·32), (A., 1921, ii, 504) The discrepancy is attributed to the effect of prolonged grindin in reducing part of the substance to the vitreous condition. Th calculated value of the heat of crystallisation at 900° is 6·50 Ca per gram-molecule. At 1300—1400°, the value is not much differer from that at ordinary temperature. J. S. G. T.

**Separation of Liquid Mixtures by Centrifuging.** ROBER S. MULLIKEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1729—1730).—I an earlier paper (this vol., ii, 492) the author showed thermo dynamically that the same separation of isotopes should be obtai able by centrifuging a liquid as a gaseous mixture, at a give speed. The same result was stated to be true for ideal solutior in general. The latter statement is now shown to be incorrec The result depends not only on the ideality of the solutions, bu also on equality of the vapour pressures and of the atomic or mol cular volumes of the constituents. These conditions are fulfille in few cases except that of a mixture of isotopes. J. F. S.

**Viscosity and Molecular Dimensions of Sulphur Dioxid** C. J. SMITH (*Phil. Mag.*, 1922, [vi], **44**, 508—511).—By Rankine method, the author has determined the viscosity of sulphur dioxid to be $1·253 \times 10^{-4}$ C.G.S. units at 18·0°, and $1·630 \times 10^{-4}$ at 100·0 The value of Sutherland's constant calculated therefrom is 41 and the corresponding value of the viscosity at 0°, extrapolate by Sutherland's formula, is $1·168 \times 10^{-4}$ C.G.S. units. The valu of the mean collision area, calculated from the results by Chapman formula, is $0·94 \times 10^{-15}$ sq. cm. with a possible error of 2 or 3%. J. S. G. T.

**Viscosity and Molecular Dimensions of Gaseous Carbo Oxysulphide.** C. J. SMITH (*Phil. Mag.*, 1922, [vi], **44**, 289-292).—The viscosities of carbon oxysulphide have been determine at 15° and 100° by the method described by Rankine and Smit (cf. A., 1921, ii, 694, 696; this vol., ii, 549). The values obtaine were $\eta_{15} = 1·200 \times 10^{-4}$ C.G.S. units, and $\eta_{100} = 1·554 \times 10^{-4}$ C.G.S units; and by extrapolation from Sutherland's formula $\eta_0 = 1·135 \times 10^{-4}$ C.G.S. units. The mean area which the molecule presen in mutual collision is $A = 1·06 \times 10^{-15}$ cm.². W. E. G.

**Measurement of the Pressure of "Surface Fluids" Acid.** A. MARCELIN (*Compt. rend.*, 1922, **175**, 346-.—In order to measure the pressure exerted by thin laye resting on the surface of a second liquid, the author h

constructed a "surface manometer" which is sensitive and capable of rapid measurement. In the case studied, the addition of successive small quantities of oleic acid to the surface of water contained in a vessel results in a corresponding increase of pressure until a limiting value is reached, at which point a portion of the acid is floating as a drop of oil on the surface. This "surface saturation pressure" is comparable with the maximum tension of saturated vapour; it characterises the equilibrium between the "surface fluid"—a two-dimensional phase—and the same substance in a three-dimensional phase. At the equilibrium point, pressure on the surface liquid results in condensation into drops, and conversely. A further series of experiments was made in which the quantity of oleic acid was insufficient to cover the entire surface of the water. By surface compression, the pressure which is initially zero increases slowly at first, then more rapidly tending towards the saturation limit, and on allowing the surface liquid to expand, its pressure decreases in the inverse sense. If curves are drawn representing these pressures as functions of the surfaces, the second curve falls below the first; the two meet asymptotically, and the whole is of the same type as the curves of magnetic hysteresis. It is also shown that there is no limit to the extension of the surface liquid; this apparently corresponds with the limitless expansion of a gas. H. J. E.

**The Properties and Molecular Structure of Thin Films. III. Expanded Films.** N. K. ADAM (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 516—531).—In continuation of previous work, the author has investigated the effect of temperature on thin films of fatty acids spread on surfaces of distilled water, a phosphate solution, a dilute solution of hydrochloric acid, and of sodium hydroxide. At a certain temperature, dependent both on the nature of the substance in the film and on the composition of the solution, the films expand along the surface. The phenomena observed are discussed at length and the attempt is made to correlate the behaviour of such expanded films with that of a gas, the barriers on the surface over which the film is expanded representing the walls of the containing vessel in the case of the gas. The "gas" equation for the expanded films is of the Van der Waals's type, the $b$ term, however, representing twice and not four times the area of the molecules, and the $v$ term being replaced by the area of the film. It is shown that expanded films are one molecule thick, and that the molecules are probably arranged vertically, that is, they do not lie flat on the surface. It is shown that the steady increase in the expansion temperature with length of chain constituting the compound probably arises owing to the lateral attraction of chains lying side by side. The bearing of this result on the crystal structure of fatty acids and their esters is discussed. There appears to be no a priori reason for the view that lateral adhesion between the molecules prevents the films dissolving. Conclusions previously reached (this vol., i, 424) regarding the structure of *cis*- and *trans*-acids are now considered to be incorrect. J. S. G. T.

**Electric Endosmose.** ALVIN STRICKLER and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1922, **44**, 1647—1662).—The rate and direction of the endosmotic flow of acetone, amyl alcohol, nitrobenzene, pyridine, benzaldehyde, *n*-butyl alcohol, furfuraldehyde, *iso*propyl alcohol, and *o*-nitrotoluene have been determined, using a modified form of Briggs's apparatus (A., 1917, ii, 236; 1918, ii, 214). The influence of the addition of acids, bases, and salts on the endosmosis has also been investigated. An adsorption orientation hypothesis has been suggested to explain the establishment of the original charge at the surface of contact of the membrane and solvent. This states that the molecules of the solvent, on adsorption, are orientated on the membrane surface producing a charge by their polarity. If dissociated molecules are present, they affect the membrane charge by specific adsorption of the ions produced. This does not eliminate adsorption, but suggests a more comprehensive view of the mechanism for the establishment of the original charge. The experiments show that the permeability of the membrane is an important factor in determining endosmotic flow, and that it is possible to use and duplicate membranes of filter-paper when using organic solvents. The rate of endosmosis is not quite a linear function of the voltage applied when this is varied over a wide range. Briggs's results (*loc. cit.*) as to temperature effects with water have been confirmed with non-aqueous solvents. The valency rule does not hold with the non-aqueous solvents investigated, and the order of adsorption of ions and their relative adsorption varies with the solvent employed. The concentration curve exhibits a maximum with non-aqueous solvents and the flow at low concentrations is in the same direction as that of the pure solvent. The addition of water to non-aqueous solutions changes the endosmosis in the direction it would manifest in pure water, the first additions showing the greatest effect. The direction of endosmosis is not determined by the dielectric constant ratio, although this is probably a measure of the magnitude of flow. The Hofmeister series is not consistent when considering endosmotic effects in non-aqueous solvents.

J. F. S.

**Dependence of the Adsorption by Charcoal on the Quantity of Charcoal and the Nature of the Adsorption Isothermal.** A. FODOR and B. SCHÖNFELD (*Kolloid Z.*, 1922, **31**, 75—80).—The adsorption of acetic, lactic, and tartaric acids by various amounts of animal charcoal from solutions of various concentration has been determined. It is shown that with sufficiently dilute solutions of these substances and with a sufficient quantity of adsorbent the index $1/n$ of the adsorption equation approaches and reaches unity in the same way as was previously shown to be the case for amino-acids, polypeptides, and some carbohydrates (A., 1921, ii, 21). In sufficiently dilute solutions the value of $n$ is very sensitive to changes in the amount of charcoal employed in the sense stated above. In less dilute solutions the value of $n$ is practically independent of the amount of charcoal used. The

*$(c_0-c)-w$ curves, where $w$ is the amount of adsorbent and $(c_0-c)$* the quantity adsorbed, are parabolic and convex to the $w$ axis and are steeper the greater the initial concentration, $c_0$, and the smaller $w$ is. The $c-w$ curves are also parabolic but concave to the $w$ axis, the concavity being greater the larger $c_0$ and the smaller $w$. From this behaviour it is concluded that the expression $dc/dw=nc/w$ is correct, and interprets the adsorption equation $x=k'(c_0-x)^{1/n}$ or $x^n=k(c_0-x)$. In keeping with this interpretation of the index $n$, the rôle of this quantity in catalytic and fermentation processes is discussed. J. F. S.

**The Adsorption of Ions.** JNANENDRA NATH MUKHERJEE (*Phil. Mag.*, 1922, [vi], **44**, 321—346).—A critical résumé of the literature on the adsorption of ions in which the author applies his theory of the origin of the charge of a colloidal particle and its neutralisation by electrolytes (cf. this vol., ii, 198). The characteristic form of the adsorption isotherm, obtained when the ions are multivalent or complex, is explained on the basis of the greater chemical activity of the complex anions over that of the simple kations. It is assumed that the electrostatic attraction of the surface on the kation is less than the chemical affinity acting on the anion. With increasing concentration of electrolytes, the charge on the surface will decrease until a balance is reached between the chemical adsorption of the anion and the electrical adsorption of the kation. The second maximum is due to a balance between the electrical adsorption of the kation and anion. A theory of the action of acids and alkalis on the surface is developed for (1) an inert surface, and (2) a chemically active surface : preferential adsorption of one ion. The maximum charge due to acids gives a measure of the hydration of the surface. The conception of the chemical adsorption of the anion is applied to ionic equilibria on the surface of colloids and to the interchange of kations in the soil. W. E. G.

**The Connexion between Hydrolysis and Adsorption.** W. MOELLER (*Z. Leder- u. Gerb.-Chem.*, 1922, **1**, 160—165, 183—188; cf. *ibid.*, 1921, **1**, 47; *Collegium*, 1920, 109, 152, 209, 267).—An investigation of the swelling and hydrolysis of gelatin in hydrochloric, acetic, lactic, and butyric acids yielded results similar to those with hide powder. Hydrolysis products with organic acids are adsorbed by the intact gelatin. With mineral acids hydrolysis, and with organic acids adsorption predominates.

CHEMICAL ABSTRACTS.

**Free Energy of Gaseous Molecules with any [possible] Partition of Velocities.** MAX PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1922, 63—70).—A theoretical paper in which the question is raised and discussed as to whether or no the free energy of a mixture of similar gaseous molecules is made up additively of the free energies of the individual groups of velocities, when the partition of velocities is anything possible and the internal energy is in accord with the temperature. It is shown that the

above question must be answered in the affirmative. It is also shown that in the diffusion of two molecular systems similar in all respects except that of velocity, the reduction of the free energy is independent of the difference in the velocities. Further, in connexion with the foregoing, it is shown how this case explains the so-called Gibbs paradox, despite the fact that the velocity is a continually changing quantity. J. F. S.

**Diffusion and Intertraction.** C. G. SCHONEBOOM (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 531—539).—The phenomenon of "pseudo-podial" intertraction was originally observed by Wright, when blood-serum was run slowly on to an aqueous solution containing from 5 to 8% of common salt. The upper fluid is carried down into the lower, and the lower rises into the upper. The phenomenon may be observed with all inorganic and organic compounds soluble in water, provided the difference in specific gravity of the two solutions is not too great and the solutions do not react chemically. Surface tension alone is concerned in the production of the phenomenon, size of molecule and water of hydration exerting no influence. Distinction is drawn between the processes of "pseudopodial" intertraction and "simple" intertraction, a process intermediate between the former and the process of diffusion. J. S. G. T.

**Preparation and Use of Collodion Osmometers.** WILLIAM BROWN (*Ann. Bot.*, 1922, **36**, 433—439).—Details are given for the preparation and use of collodion thimbles for osmotic experiments. They are adapted for comparative rather than for absolute measurements. G. W. R.

**Ionic Properties and Chemical Facts. IV. Lattice Energy and the Work of Ionisation of Inorganic Compounds.** H. G. GRIMM (*Z. physikal. Chem.*, 1922, **102**, 113—140; cf. this vol., ii, 127, 483, 635).—A theoretical paper in which the author has collected and calculated the necessary data for comparing the regularities of the heat of formation of inorganic substances, and for showing the connexion between the heat of formation with the ionic properties, charge, radius, and structure. The lattice energy and work of ionisation have been calculated or approximated for about one hundred inorganic substances from the newer experimental data and where this is not available the differences of the lattice energy have been measured and the variation thus determined. J. F. S.

**Ionic Properties and Chemical Facts. V. Connexion between Heat of Formation, Lattice Energy, and the Ionic Properties.** H. G. GRIMM (*Z. physikal. Chem.*, 1922, **102**, 141—168; cf. preceding abstract).—The connexion between the heat of formation, lattice energy, ionic radius, ionic structure, and ionic charge has been investigated. It is shown that, in opposition to the heat of formation, the lattice energy of solid substances and the work of ionisation of gaseous substances, so far as these are practical, are definitely related to the ionic properties, charge, [illegible], and radius. The lattice energy and work of ionisation

ecrease with increasing radius both with anions and kations ·hen the ions compared have the same number of exterior electrons. 'he characteristic gradation of the ionic radii is in general repro- uced in the gradation of the lattice energy. The difference etween the lattice energies of compounds of two outwardly similarly onstructed kations or anions with a common anion or kation ·ith the same exterior sheath, decreases with increasing radius of the ommon ion. Compounds which contain kations with eighteen xterior electrons have considerably greater lattice energies than ompounds with the corresponding kation of the same period hich have only eight electrons. The haloids of kations with ighteen or twenty exterior electrons show a much smaller depend- nce of the lattice energy on the halogen-ion radius than the haloids f kations with eight exterior electrons. In all cases investigated he series $U_{H^+} > U_{Li^+} > U_{Na^+}$ is true, where $H^+$ has 0, $Li^+$ has 2 and $Na^+$ has 8 exterior electrons. The empirical relationship $(U_{(SiX'_4)} - U_{(SiX''_4)})|4 > (U_{(AlX'_3)} - U_{(AlX''_3)})|3 > U_{(NaX')} - U_{(NaX'')}$ is shown to be rue, where $U$ represents the work of ionisation of the substance 1 the brackets and X′ and X″ are halogens. A similar expression s also true for boron and lithium haloids. These relationships an be deduced when heteropolar linkings are assumed for all the ubstances concerned. The haloids of carbon and the halogen- ubstituted hydrocarbons do not follow a relationship corresponding ·ith that followed by ions containing the helium sheath. This ıdicates, as also do preliminary and approximate calculations on he models of $BH_3$ and $CH_4$, that the carbon compounds concerned o not possess a polar linking. Making use of Born's cycle, many f the known regularities of the heat of formation of solid substances nd of dissolved substances as well as the exceptions to the regul- rities can be investigated. The gradation of the heat of formation y the variation of a single ion of the compound can be attributed o the variation of three thermochemical quantities which depend n the ionic properties in the simplest manner. The periodicity f the heat of formation of oxides and chlorides can, in the neigh- ourhood of the maxima and minima, be explained by similar nalysis.

J. F. S.

**Effect of Sucrose on the Activities of the Chloride- and Iydrogen-ions.** J. W. CORRAN and W. C. McC. LEWIS (*J. Amer. Chem. Soc.*, 1922, **44**, 1673—1684).—The effect of the ddition of sucrose on the activity of the chloride-ion in 0·1*N*- and ·5*N*-solutions of potassium chloride solutions has been investigated y means of the cell $Ag|AgCl|KCl(c_1)||KCl(c_2)+Sucrose|AgCl|Ag$. t has been found that the increase in activity could be accounted or by simply taking account of the decrease in the total water resent in the solutions; that is, the potassium- and chloride-ions re soluble in the water of hydration of the sucrose. The effect f sucrose on the activity of the hydrogen-ion in 0·1*N*-hydrochloric cid has also been investigated, making use of the assumption of MacInnes (A., 1919, ii, 385) of the independent activity of the hloride-ion in solutions of chlorides of the same concentration.

It is shown by means of a comparison between the hydrogen-ion activities obtained in the present experiments, and the values obtained with a hydrogen electrode, that the hydrogen electrode measures the hydrogen-ion activity and not the geometric mean of the activities of the hydrogen-ion and the accompanying anion.

J. F. S.

**Ionisation Constant of Hypochlorous Acid: Evidence for Amphoteric Ionisation.** WILLIAM A. NOYES and THOMAS A. WILSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1630—1637).—The electrical conductivity of dilute solutions of hypochlorous acid and mixtures of nitric acid and hypochlorous acid at 25° was measured, using a flowing electrolyte, with the object of testing the view of *Stieglitz (A., 1902, ii, 66) that hypochlorous acid is an* amphoteric electrolyte. The results show that the value $k_a$ is $6{\cdot}70 \times 10^{-10}$, the value of $k_b$ for hypochlorous acid is too small to be determined by the change in the conductivity of $0{\cdot}0001N$-nitric acid when hypochlorous acid is added to it. When a current of air is passed through a solution of hypochlorous acid, chlorine monoxide and not the acid escapes. This indicates the presence of positive chlorine-ions in such a solution and confirms the amphoteric ionisation of the acid; $HClO \rightleftharpoons H^{\cdot} + ClO'$; $HClO \rightleftharpoons Cl^{\cdot} + OH'$. If the Lewis-Langmuir *hypothesis is accepted, it requires an interpretation consistent with these facts.* J. F. S.

**State of Aggregation and Liquid Crystals.** O. LEHMANN (*Z. physikal. Chem.*, 1922, **102**, 91—101).—In a recently published work ("Die Aggregatzustände") Tammann has qnestioned the existence of liquid crystals because they do not fall into the scheme of states of aggregation. The author, therefore, has repeated the evidence on which the existence of the liquid crystal state of aggregation is based. J. F. S.

**Glass Suspensions produced by Rubbing Glass Walls with Glass Rods.** ROBERT FRICKE (*Kolloid Z.*, 1922, **31**, 80—81).—Moderately concentrated glass suspensions may be prepared by rubbing the sides of a test-tnbe with a glass rod. These suspensions are alkaline to phenolphthalein and have a normality of the order 1/1000 which increases on keeping the suspension. They generally settle completely in twenty-four hours, but the settling is more rapid if electrolytes are added. The particles are negatively charged and wander to the anode on the application of an electric current. Examined in the ultramicroscope, the particles are seen to have diameters varying between 20 $\mu$ and 0·5 $\mu$.

J. F. S.

**A New Apparatus: The Nephelectrometer.** I. NEWTON KUGELMASS (*Compt. rend.*, 1922, **175**, 343—345).—Changes in the degree of aggregation of a colloidal solution may be observed quantitatively by measuring variations in the degree of transparency. This is effected by allowing light of weak intensity from a constant source to fall on a sensitive thermopile after traversing a vessel containing the solution. The apparatus is

standardised by taking a series of readings after filling the vessel with distilled water. The author has used the apparatus in order to observe the coagulation of fibrinogen and the results obtained are expressed numerically. H. J. E.

**Nephelometric Effect of Colloidal Systems of Different Size of Particles.** H. BECHHOLD and F. HEBLER (*Kolloid Z.*, 1922, **31**, 70—74).—The connexion between the turbidity and size of the suspended particles has been examined nephelometrically in the case of suspensions of barium sulphate in various mixtures of ethyl alcohol and glycerol. The degree of dispersion of the suspensions varied from 2·5 μ to 4 μμ. The results show that for suspensions containing the same amount of barium sulphate but of varying degrees of dispersion, the turbidity increases from 2·5 μ downwards. The maximum turbidity is reached with particles of about 800 μμ for white light, that is, in the region of the extreme red. Further reduction of the size of the particles caused the turbidity to decrease strongly. It is in this region that Rayleigh's law holds. By the term turbidity is to be understood the effect, observed with the nephelometer, which is brought about by the diffraction of the light by the disperse phase. A method is described whereby the diameter of submicrons and amicrons may be determined if a comparison turbidity of a substance with particles of known diameter is available. J. F. S.

**Turbidity Standard.** H. BECHHOLD and F. HEBLER (*Kolloid Z.*, 1922, **31**, 132—137).—The authors have prepared an easily reproducible and fairly stable standard turbidity and a sol suitable for use as a standard in work on turbidities and suspensions. They characterise as standard turbidity one which contains 1/1000 mol. of barium sulphate; this is prepared by mixing 1/500 mol. of hydroxylamine sulphate dissolved in glycerol with an equal volume of 1/500 mol. barium chloride also dissolved in glycerol. The precipitate is chiefly made up of particles 2·5 μ in diameter. The standard sol is characterised as a turbidity which contains 1/200 mol. of barium sulphate; this is prepared by mixing barium chloride and magnesium sulphate dissolved in a mixture of glycerol (6·5) and *iso*butyl alcohol (1·5). This is three times as turbid as the standard turbidity and can be made of the same turbidity by mixing with glycerol containing 15% of *iso*butyl alcohol. The standard sol consists of primary particles of not more than 90 μμ diameter. The standard sol is stable and constant for at least six months, whilst the standard turbidity is not trustworthy after eight days. J. F. S.

**Theory of the Mechanical Synthesis of Colloids.** F. SEKERA (*Kolloid Z.*, 1922, **31**, 137—147).—The theory of the production of colloids in Plauson's colloid mill is briefly as follows. The mechanical grinding process bursts the active molecular compounds in the interior of the solid substance and produces particles of colloidal dimensions. From the surface of these particles the residual valencies tend to cause an aggregation of the small particles, so that secondary to the dispersion an aggregation process

is taking place. To retard or prevent the aggregation, the residual valencies are saturated by the addition of an electrolyte which produces salt complexes and charges the particles. J. F. S.

**Dielectric Constants of Colloidal Solutions.** J. ERRERA (*Kolloid Z.*, 1922, **31**, 59—64).—A method for measuring the dielectric constants of colloidal solutions, based on the Nernst condenser method is described and has been used to measure the dielectric constant of vanadium pentoxide sols. It is shown that a solution containing 14 per thousand has a dielectric constant of 400 in comparison with that of water of 81. This high value is not obtained with the freshly prepared sol, but appears only after long preservation. Thus a freshly prepared sol gave value 74·7 which in seventeen days had risen to 94·8. The value given above was for a sol which had been kept for five years. The dielectric constant shows a characteristic dilution curve and definite dependence on the temperature, current density, and the potential amplitude. The dielectric constant obtained is doubtless connected with the well-known double refraction of this sol.

J. F. S.

**An Experimental Test of Smoluchowski's Theory of the Kinetics of the Process of Coagulation.** JÑANENDRA NATH MUKHERJEE and B. CONSTANTINE PAPACONSTANTINOU (*Phil. Mag.* 1922, [vi], **44**, 305—320).—According to the theory of Smoluchowski (cf. A., 1917, ii, 297), the successive stages in the coalescence of a colloidal solution are always the same and depend only on the time, and thus any property of the sol that varies continuously can be utilised to fix a definite stage in the coalescence. If his equations hold, all curves showing variations in the physical properties of the colloidal solution should be similar. Previous experimental work in which ultramicroscopical measurements have been made has yielded inconclusive data, possibly owing to difficulties inherent in the methods of measurement. The authors have tested the views of Smoluchowski by measurements of the changes in colour of gold sols on the addition of an electrolyte (cf. T., 1920, **117**, 1563). Since the absorption coefficient in the red region varies continuously with the coagulation, the attainment of a definite value of the absorption coefficient for a fixed wave length (683 $\mu\mu$) is taken as representing a definite stage in the coalescence. Experimental values of the absorption coefficient for the addition of several concentrations of potassium chloride, potassium nitrate, and barium chloride have been previously given (*loc. cit.*), and it is shown that the ratios of the times required to reach the same absorption coefficient are independent of the time or the stage of coalescence. The data thus supply the best evidence so far recorded in favour of the theory of Smoluchowski. $T$ in his equations is a constant in the case of the gold sols within the limits of coagulation studied. The percentage of successful collisions between the colloidal particles increases rapidly with increase in concentration of electrolyte and varies markedly with changes in temperature. W. E. G.

**Colloidal Solutions of Carbon in Water.** P. C. L. THORNE (*Kolloid Z.*, 1922, **31**, 119—132).—The author briefly summarises the literature on the formation of colloidal solutions of carbon and discusses the results obtained. An account is given of the preparation of colloidal solutions of carbon by the dispersion of charcoal anodes in the electrolysis of solutions of ammonia, sodium hydroxide, and dilute acids; similar experiments were carried out with graphite electrodes. A stable carbon sol may be prepared by the electrolysis of a solution of ammonia for six hours between two carbon electrodes with an anode current density of 0·6—1·2 amperes/cm.$^2$ and a voltage of 220. On filtering, the solution had a concentration 0·145*N* of ammonia and gave a residue of 0·034 gram per 100 c.c. This residue was insoluble in water, but redissolved in a dilute solution of ammonia; the excess of ammonia may be removed by boiling and the sol is then more stable than one which has been dialysed and still contains 0·039*N* ammonia. The ammonia-free sol is deep black in layers greater than 1 cm. thick and in thinner layers brown, and is made up of particles of about the same size as those of metallic sols. The influence of electrolytes on the sol has been investigated and the number of millimols. necessary to coagulate 1000 c.c. of the dialysed sol found to be: hydrochloric acid, 60; sodium hydroxide, 290; ammonium hydroxide, >9000; sodium chloride, 450; barium chloride, 0·5; and aluminium chloride, 0·3. These quantities are very similar to those required to coagulate a platinum sol. Similar experiments have been carried out with graphite sols and results of the same kind obtained. The most marked difference between the carbon sols and the graphite sols is that of colour, the former being brown and the latter black. An analysis of the dried sol shows that it is not a pure carbon sol which has been dealt with, but a mixture, the composition being C, 66·61%; H, 1·99%; O, 15·25%, insoluble and incombustible residue (probably silica), 16·15%. J. F. S.

**Electrical Properties of Silicic Acid Sols.** OTTO LÖSENBECK (*Koll. Chem. Beihefte,* 1922, **16**, 27—46).—A number of experiments are described on the influence of silicic acid sols on the electrical conductivity of solutions of hydrochloric acid, and on the kataphoresis of the sol both pure and in the presence of hydrochloric acid of various concentrations. It is shown that the electrical conductivity of hydrochloric acid solutions of concentrations up to 0·01*N* is considerably reduced by the presence of silicic acid sol. This reduction does not take place instantaneously, but the amount of decrease increases with time according to a function of *e*, that is, the decrease is at first rapid and then continuously slower until it becomes asymptotic and a limiting value is approached. From the measurements of the migration velocity of the silicic acid particles under a known potential fall, the contact potential has been calculated by means of Smoluchowski's theory. It is shown that the particles of a pure silicic acid sol are negatively charged and that the charge is steadily reduced by the addition

of hydrochloric acid until the isoelectric point is reached. With further addition of acid the sign of the charge changes and the charge increases until the positive value is greater than the original negative value. The silicic acid particles are shown not to be uniform. The contact potential of the particles determined in different concentrations of the same preparation shows that this quantity is dependent on the concentration of the sol, in the sense that the isoelectric point of different sols lies at greater concentrations of hydrochloric acid the greater the concentration of the sol. The observed results are explained by the assumption that the silicic acid particles are saturated with hydrochloric acid, like a sponge, and that this is taken up slowly. The hydrogen-ions are expelled from these sponges with a definite tension, so that the contact potential between particle and solution may be approximately represented by the Nernst formula. J. F. S.

**Colour of Photochlorides and Colloidal Silver. II.** KARL SCHAUM and THEODOR MARX (*Kolloid Z.*, 1922, **31**, 64—70; cf. A., 1921, ii, 506).—In a previous paper (*loc. cit.*) the authors describe the presence of faintly illuminating red particles in silver sols of medium dispersion; these particles do not conform to Mie's theory. The authors now show that the red particles do not exist and the red colour observed was due to a contrast with the many green particles present. A method of determining the true colours of the colloidal particles in the presence of other particles is described. Previous attempts to reverse the order of colours obtained in photographic intensification by reduction failed, but it is now shown that a complete reversal may be obtained as follows. A blue silver sol is mixed with an equal volume of 10% gelatin solution and allowed to solidify, then a concentrated solution of ammonium hydroxide, potassium cyanide, or sodium thiosulphate is poured on to it and allowed to diffuse. After several days the following range of colours is observed, commencing at the top of the tube: colourless, yellow, orange, red, reddish-violet, bluish-violet, and blue. The action of electrolytes in definite amounts on silver sols is to produce definite colours. Thus in the case of magnesium sulphate and silver sols, 2 c.c. of the sol when treated with the following quantities of $N/20$-magnesium sulphate gives the colours indicated: 0 c.c., yellow; 0·10 c.c., orange; 0·20 c.c., red; 0·25 c.c., purple; 0·30 c.c., reddish-violet; 0·50 c.c., bluish-violet; and 1·50 c.c., blue. Similar changes were also obtained with ammonium chloride, sodium chloride, and potassium sulphate. J. F. S.

**Behaviour of Carey Lea's Silver Sol towards Electrolytes and Hydrophilic Colloids.** H. FREUNDLICH and E. LOENING (*Koll. Chem. Beihefte*, 1922, **16**, 1—26).—Carey Lea's silver sol behaves as an entirely hydrophobic sol, and since its particles are negatively charged the valency of the kations and the adsorbability are of most importance in its coagulation. The dependence of the coagulation value on the concentration of silver micellæ is bound up with the valency of the kations. The coagulum has a quite

different appearance when it is produced by univalent kations from that prodnced by bi- and ter-valent kations. Hydrophilic colloids such as saponin and gum arabic exert a protective action at all concentrations. This action increases strongly with the concentration of the hydrophilic colloid in the coagulation by tervalent kations, less strongly with bivalent kations, and weakly with univalent kations. This is explained by the fact that with the tervalent kations much smaller concentrations are necessary, so that the displacing action of the protective colloid is made more noticeable. Other hydrophilic colloids such as gelatin and caseinogen in smaller concentrations coagulate the silver sol, but above a definite concentration exert a protective action; this concentration increases with the concentration of the silver micellæ in the sol. The coagulation with small concentrations is, in the main, similar to the coagulation of acid gold sols by hydrophilic sols investigated by Gann (A., 1917, ii, 21). In neither case need complete coagulation occur, and an increase in the sensitiveness is brought about, that is, the metallic sol which contains small quantities of the hydrophilic colloid, is more sensitive toward electrolytes than the pure sol. Coagulation and increase in the sensitiveness by means of hydrophilic colloids are due to the fact that the sols of the hydrophilic colloids contain ions. In the case of the negative metallic sols, the colloid kations are operative and coagulate in the same manner as other kations. The silver sol is not discharged in solutions of colloids such as gelatin and caseinogen which are concentrated enough to exert a protective action, but here it is negatively charged. Tbis is explained by the assumption that the amphoteric ions of gelatin lie with their positive ends toward the silver particles and the negative ends toward the interior of the solution. The above explanations are in keeping with the facts, that gelatin behaves in a protective but non-coagulating manner toward an alkaline gold sol, because even in alkaline solutions it contains too few colloidal kations; on the other hand, clupein sulphate, a protamine salt, which contains definite colloidal kations, coagulates an alkaline gold sol strongly. J. F. S.

**Influence of Temperature on the Coagulation of Colloidal Gold.** H. Lachs and Stephanie Goldberg (*Kolloid Z.*, 1922, **31**, 116—119).—The time required for the coagulation of gold sols prepared in various ways by a constant amount of sodium chloride has been determined at temperatures up to 70°, and in this way the influence of temperature on the rate of coagulation ascertained. The results show that the influence of temperature corresponds with that demanded by Smoluchowski's hypothesis, namely, that the coagulation time is inversely proportional to the absolute temperature. The sensitiveness, toward temperature changes, of the coagulation of colloidal gold is very much smaller than that of chemical reactions. J. F. S.

**The Kinetics of the Coagulation of Proteins by Heat.** Heinrich Lüers and Max Landauer (*Z. angew. Chem.*, 1922, **35**, 469—471).—The velocity of coagulation of the plant albumin,

leucosin, was determined by the direct weighing of the coagulu produced at intervals during the reaction. The change of hydroge ion concentration during the reaction was very slight. It w concluded that the coagulation occurs in two stages; a chemic denaturation process followed by a colloidal phenomenon coagulation, which is a flocculation of the denatured prote particles. The denaturation of the leucosin particles was shov to be a chemical reaction of the first order. The temperatu coefficient of the denaturation in a medium of $p_H$ 6·09 and at ter peratures between 52·90° and 57·05° was 1·47 per 1°. A. G. P.

**Is the Gelatin–Gum Arabic Coagulation a Chemical or Colloid-chemical Process?** F. W. Tiebackx (*Kolloid Z.*, 192 **31**, 102—103).—A discussion of the coagulation of gelatin–gu arabic mixtures by acids, alkalis, and salts, from which it is shov that the coagulation is a mixed process which can be regarded in part of a chemical nature and in part of a colloid-chemical natur J. F. S.

**Influence of Substituents on Various Chemical Reaction** Sven Bodforss (*Z. physikal. Chem.*, 1922, **102**, 40—53).—It h been shown previously (A., 1918, i, 229) that a number of su stituted aromatic aldehydes react with bromoacetophenone the presence of sodium ethoxide according to the equatior $Ph{\cdot}CHO + CO{\cdot}Ph{\cdot}CH_2Br \longrightarrow CO{\cdot}Ph{\cdot}CH{\cdot}CH{\cdot}C_6H_5$ (with $>O<$ bridging the two CH groups), whilst others c not react in this way. The aldehydes which react all contain negative substituent and those which do not may be brought t react by substituting such a negative group in them. It is no shown that the acids produced from the aldehydes which rea are stronger than those produced from the aldehydes which c not react. The relationship between the reactivity of the ald hydes and the strength of the corresponding acid has been i vestigated. The strength of a number of substituted benzo acids has been determined from conductivity measurements an the dissociation constant compared with the values for oth acids found in the literature. The following newly determine values of $K$ at 25° are recorded: 3-nitroanisic acid, $1{\cdot}9\times10^{-}$ 3-bromoanisic acid, $7{\cdot}2\times10^{-5}$; cumic acid, $5{\cdot}2\times10^{-5}$; piperonyl acid, $4{\cdot}5\times10^{-5}$. A further series of experiments has been carrie out to ascertain the relationship between the maximum work a given type of reaction and the nature of the substituting grou The reaction chosen is represented by the equation H+AgBz(solid)= HBz(solid)+Ag and the maximal work of this reaction has bee calculated from *E.M.F.* measurements of cells of the type A AgBz,HBz(solid)|HBz(solid)|$H_2$ and Ag|AgBz(solid)||HBz(solid Quinhydrone|Pt. at 25° (cf. Biilmann, A., 1921, ii, 372). Th following values of the *E.M.F.* ($\pi$), the maximum work ($A$ cal. and the dissociation constant, respectively, are recorded 5-nitrosalicylic acid, 0·066, 1520, $8{\cdot}9\times10^{-3}$; salicylic acid, 0·08 2010, $1{\cdot}0\times10^{-3}$; *m*-nitrobenzoic acid, 0·109, 2510, $3{\cdot}5\times10^{-}$ 3-nitroanisic acid, 0·135, 3110, $1{\cdot}9\times10^{-4}$; anisic acid, 0·144, 332

$3{\cdot}2\times10^{-5}$; *m*-nitrocinnamic acid, 0·145, 3340, $8{\cdot}3\times10^{-5}$; *o*-chlorobenzoic acid, 0·147, 3390, $1{\cdot}3\times10^{-3}$; benzoic acid, 0·154, 3550, $6{\cdot}7\times10^{-5}$; *p*-nitrobenzoic acid, 0·160, 3690, $4{\cdot}0\times10^{-4}$; 3-bromoanisic acid, 0·163, 3760, $7{\cdot}2\times10^{-5}$; and piperonylic acid, 0·165, 3800, $4{\cdot}2\times10^{-5}$. The above results show that generally the maximum work decreases with increasing dissociation constant. The cases where this relationship is not strict are probably to be explained either by the formation of hydrates by the silver salts or by the formation of acid silver salts. J. F. S.

**Equilibrium in Heterogeneous Systems.** JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 161—165).—Investigation of the reaction $CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4$ with concentrations ranging from 0·01 to 0·002 gram-mol. per litre and thus corresponding with widely varying degrees of dissociation of the component salts, shows that the reaction does not conform to the law of equilibrium, the "constants" of the reaction exhibiting wide divergences. The reaction is reversible, the reversibility, that is, the proportion of non-reacting molecules, amounting to 58% at the ordinary temperature and at low concentrations. At 7°, scarcely any action occurs. The value of the reversibility at 38° is similar to that at 18°, probably owing to the solubility of calcium sulphate being at a maximum at 38°. The reversibility is a function of the concentration and increases with dilution, the more rapidly at low temperatures.

Thus, with reactions involving the formation of a new phase, the laws of equilibrium are incomparably more complex than with homogeneous reactions. At present, the dependence of the reversibility on the concentration is expressible only by an empirical relation of the form $Z=1+ac+bc^2$. . . . T. H. P.

**The Equilibria in Aqueous Solutions of the Alkali Metal Bisulphites.** EDWARD CHARLES CYRIL BALY and ROBERT ARTHUR BAILEY (T., 1922, **121**, 1813—1821).

**Equilibria and Reaction Velocities.** W. F. BRANDSMA (*Chem. Weekblad*, 1922, **19**, 318—322).—The treatment of reaction velocities based on molecular collisions of substances in the gaseous state or in dilute solution becomes difficult when the course of a reaction is not expressed by a simple equation, and experimental results do not agree with theory. The conditions leading to equilibrium may be regarded from two points of view, the first dealing with the forces involved, that is, the energy units, and the second with space factors, that is, with entropy units. The factors deduced from the first vary inversely with the absolute temperatures, and so determine the temperature coefficients; the entropy factors are independent of temperature.

This division is of great importance in organic reactions, since the theoretical treatment can take due account of both energy and space factors. S. I. L.

**Theory of the Velocity of Chemical Reactions.** J. N. BRÖNSTED (*Z. physikal. Chem.*, 1922, **102**, 169—207).—A theoretical

paper in which the laws of the velocity of chemical reactions ar considered. It is shown that chemical reactions between neutra molecules, or between neutral molecules and ions, are norma that is, they follow very closely the law of mass action and ar insensitive or only slightly sensitive to the addition of a neutra salt. Reactions between ions are abnormal, that is, the velocit constant is to a high degree dependent on the concentration c the reacting ions and on the concentration of an added neutra salt. For thermodynamical reasons, the concentrations or osmoti partial pressures in the ordinary kinetic reaction equations ar to be replaced by the activities, and the equations are then true whe the activities alone are changed. The reaction determinative of th velocity in a chemical change consists of the formation of an unstabl critical complex in the sense put forward by Marcellin (A., 1915 ii, 328). The electrical charge of the complex is the sum of th charges of the reacting molecular species. The regularities an exceptions mentioned above are to be explained by the assumptio that the velocity is inversely proportional to the activity coefficien of the critical complex, and that this is influenced by changes in th salt concentration in the same way as the ordinary ions. The dat concerning the activity coefficients necessary for calculating th anomalies in the velocity are most easily obtained from solubilit determinations of sparingly soluble salts in solvents containin dissimilar ions. The dependence of the activity coefficient on th concentration, obtained in this way, for the ions of various type makes it possible to calculate the extent of the neutral salt action, that is, the kinetic anomalies for the various types of reactions. On the basis of the foregoing, the following theoretical result is obtained. In reactions between ions of the same sign the salt action is positive, that is, the velocity is increased by an increasing salt concentration. In reactions where the reacting ions have opposite signs, the salt action is negative, that is, the reaction is retarded by increasing salt concentration. These theoretical results have been applied to a large number of chemical reactions in solution and for the greater number found to be confirmed, in some cases quantitatively. The kinetic and static anomalies may be removed by employing a concentrated solution of an indifferent salt as solvent. J. F. S.

**Velocity of Decomposition of Crystalline Substances.** A. Sieverts (*Z. physikal. Chem.*, 1922, **102**, 89—90).—An answer to Hinshelwood and Bowen (this vol., ii, 628; see also this vol., ii, 360; A., 1920, ii, 743; 1921, ii, 443). J. F. S.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Foundation. III. Reaction between Manganate and Formic Acid.** Josef Holluta (*Z. physikal. Chem.*, 1922, **102**, 32—39; cf. this vol., ii, 448, 628).—The velocity of the an?tion between sodium manganate and sodium formate has been 5-nitpined at temperatures varying between 27·4° and 22·6°, with 2010, 't concentrations of manganate and hydroxyl-ion and also 3-nitroaring concentrations of all constituents. The results show

that the reaction as measured is of the second order, and is to be represented by the equation $MnO_4'' + HCO_2' + 2H_2O = Mn(OH)_4 + CO_3'' + OH'$. Intermediate stages therefore do not need to be taken into account in the mechanism of this reaction. J. F. S.

**Dependence of the Velocity of Alkaline Hydrolysis of Esters on the Constitution of the Alcohol. I.** L. SMITH and HUGO OLSSON (*Z. physikal. Chem.*, 1922, **102**, 26—31).—The alkaline hydrolysis of propyl acetate and *iso*propyl acetate by $0·1145N$-sodium hydroxide has been determined at 20°. The reaction constants are found to be 4·23 and 1·263, respectively, giving as the ratio between the propyl and *iso*propyl esters the value 3·4, a value which is very near the value (3·2) found by Menschutkin for the ratio of the rates of formation of the two esters.

J. F. S.

**Catalysts and Chemical Equilibrium.** J. F. DURAND (*Bull. Soc. chim.*, 1922, [iv], **31**, 759—762).—The conclusions drawn by Clarens (this vol., ii, 436) with regard to the effect of catalysts on the equilibrium of a system are criticised. H. J. E.

**Catalytic Formation of Water Vapour from Hydrogen and Oxygen in the Presence of Copper and Copper Oxide.** ROBERT N. PEASE and HUGH S. TAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 1637—1647; cf. this vol., ii, 148).—The catalytic combination of hydrogen and oxygen in the presence of metallic copper (produced by the reduction of copper oxide in hydrogen at 150—200°) has been investigated over the temperature range 100—200°, using gaseous mixtures containing up to 5% of oxygen. The results show that combination is practically complete at 200°, and is just measurable at 100°. In nearly all cases, copper oxide is formed simultaneously with water. After the oxygen is shut off and pure hydrogen alone passed over the catalyst, the oxide so formed is reduced at a greater rate than that of the formation of water while the oxygen is passing. Between 130° and 100°, the rate of oxidation of the copper and the rate of reduction of the oxide so formed, as well as the catalytic activity, suffer a marked reduction. At 130°, with oxygen equivalent to 10 milligrams of water passing in five minutes, the rate of formation of water passes through a maximum to a steady minimum value. The above results are satisfactorily explained by assuming that the combination takes place mainly as a result of the alternate oxidation and reduction of the catalyst, the reduction reaction being complicated by the known inhibitory influence of free oxygen on that reaction. J. F. S.

**Catalysis of Hydrogen Peroxide by Finely Divided Platinum. The Influence of Inhibitants.** EDWARD BRADFORD MAXTED (T., 1922, **121**, 1760—1765).

**Bohr and Langmuir Atoms.** (SIR) OLIVER LODGE (*Nature* 1922, **110**, 341).—In view of the difficulty of explaining molecular combination in terms of electrical attraction between revolving electrons composing the peripheral parts of an atom (in accordance with

the demands of spectroscopic observations) rather than in terms of a static arrangement (more suited to the facts of chemical combination), it is considered that the idea of electrical attraction between the atoms as the major chemical force should give place to that of the interlacement of the magnetic fields which inevitably accompany rapidly revolving electric charges. A. A. E.

**The Neuburger Nuclear Model.** F. PABLO VALERAS (*Physikal. Z.*, 1922, **23**, 304—305).—The relative merits of the Neuburger (cf. this vol., ii, 208, 365) and Meitner (cf. *ibid.*, ii, 15) models are discussed and an objection is raised to the latter model since it cannot be applied to the nuclei of boron[10], boron[11], nitrogen, or fluorine. The Neuburger model is unsatisfactory, since it requires the existence of *iso*helium nuclei. The author proposes a new model in which the nuclear formulæ are given by $F_k = n\alpha + pH^+ + v\beta$ which takes account of all known atoms. W. E. G.

**The Neuburger Nuclear Model.** LISE MEITNER (*Physikal. Z.*, 1922, **23**, 305).—A reply to Pablo Valeras (preceding abstract), pointing out that the new model is not in agreement with radioactive phenomena. W. E. G.

**The Neuburger Nuclear Model.** MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 305—307).—A reply to F. Pablo Valeras (cf. preceding abstracts). The assumption of the existence of the *iso*helium nucleus is useful in explaining the structure of $Gl^9$ which cannot be expressed by the new model. A schematic representation is given of the structure and genesis of some of the lighter atoms. W. E. G.

**The Stability of Atom Nuclei, the Separation of Isotopes, and the Whole Number Rule.** WILLIAM D. HARKINS (*J. Franklin Inst.*, 1922, **194**, 165—211; cf. A., 1915, ii, 543, 544, 814; 1920, ii, 479, 541).—The author has pointed out that of the first twenty-seven elements except hydrogen the atomic weights are very close to whole numbers on the basis of O=16, and those of which the atomic weights are multiples of 4 are much closer to whole numbers than the others. The simple explanation is that all the elements are intra-atomic compounds of hydrogen and that whilst in molecular compounds the latter has the atomic weight 1·0078, in these much closer combinations it has the atomic weight 1·000. Those atoms of which the atomic weights are divisible by 4 are regarded as being built up of α-particles which are known to be the nuclei of helium atoms. A system of notation denoting the electronic structure of the atoms has been introduced; for example, "Oxygen=16" is written $p_{16}e_{16}$ as a compound of 16 positive and 16 negative electrons. This is further elaborated to show the number of α-particles ($a$) present in the nucleus, and negative electrons in the nucleus are differentiated from those in the planetary system. The nuclei of elements of even atomic number can be represented as built up in this way of α-particles alone or with "cementing" negative electrons, usually two in

number. Those of odd number cannot be so represented but need the introduction usually of a "proton-electron" group, $p_3e_2$.

From a consideration of the composition of meteorites, the earth's crust, and the radioactive series, the conclusion is drawn that the elements of even atomic number are much more stable than those which are odd. The atomic numbers of the five undiscovered elements are all odd. The stability is attributed to the great stability of the α-particle in the nucleus. The special relativity theory is used to explain the loss in weight of the four hydrogen atoms (4×1·0078) which form the helium atom (4·000), and the energy freed by this loss is shown to be $6·708\times10^{11}$ cals. per gram-atom of helium formed. This theory is also applied to the calculation of weight losses in radioactive disintegrations, and it is shown that an experimental determination of the loss of mass of radiothorium over a period of three years would be a check on the validity of the theory. A. C.

**Model of the Ionised Hydrogen Molecule.** W. Pauli, jun. (*Ann. Physik*, 1922, [iv], **68**, 177—240).—A mathematical investigation of the conditions determining the stability of a model representing the motion of an electron under the influence of two positively charged nuclei, at rest and in equilibrium, a structure illustrating the ionised hydrogen molecule $H_2^+$ met with in positive rays. The analysis is based on an application of the quantum theory, and the extension of Bohr's correspondence principle to impacts between atoms or molecules and free electrons. Various orbits are investigated. Of quantised orbits symmetrical with regard to the medium plane bisecting at right angles the line joining the nuclei, that of minimum energy is characterised by three quantum numbers, 0, 1, 1, and fills up in a uniform manner the space contained within an ellipsoid of revolution. The possibility of the existence of a stable unsymmetrical quantised orbit remains for the present open. Consideration of the value of the ionisation potential of the hydrogen molecule indicates that the structure of the ionised hydrogen molecule is essentially meta-stable, and it is concluded that its real normal representation consists of an electron moving in a circular orbit in the medium plane between the nuclei, and characterised by conditions of stability and energy similar to those of the earlier Bohr model of the helium atom. Preliminary remarks are made concerning the application of the theory to the band emission spectrum of the ionised hydrogen molecule.

J. S. G. T.

**The Mathematics of the Dicyclic Colour Theory, and a New Theory of the Structure of the Nitrogen Atom.** James Moir (T., 1922, **121**, 1808—1813).

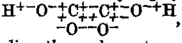
**The Distribution of Electrons around the Nucleus in the Sodium and Chlorine Atoms.** W. Lawrence Bragg, R. W. James, and C. H. Bosanquet (*Phil. Mag.*, 1922, **44**, 433—449).—The distribution of electrons in the atoms of sodium and chlorine has been determined by measuring, by the method of *X*-ray analysis, the reflecting power per unit volume of the units constitut-

ing a crystal of sodium chloride. The experimental results indicat that the sodium atom comprises seven electrons arranged on a shell of radius 0·29 Å. and three electrons on a shell of radius 0·76 Å The chlorine atom comprises ten electrons arranged on a shell o radius 0·25 Å., five electrons on a shell of radius 0·86 Å., and thre electrons on a shell of radius 1·46 Å. Alternatively, the result are interpreted by continuous curves in which the electron densit is plotted as ordinate against the corresponding distance of th electron from the centre of the atoms as abscissa. Considerabl agreement is found between the experimentally determined value of the distribution factor $F$ and those calculated for an atom of th type proposed by Bohr and comprising two electrons describin circular one-quantum orbits of radius 0·05 Å., four electron describing two quantum circular orbits of radius 0·34 Å., and fou electrons describing two-quantum elliptical orbits of semi-majo axis 0·42 Å. The principal source of error in the conclusions arise owing to lack of information as to the part played by "extinction" in affecting the intensity of $X$-ray spectra. The results indicat that there cannot be, either in the sodium or chlorine atom, an outer shell of eight electrons. Eight electrons revolving in circula orbits of the same radius are equally inadmissible. J. S. G. T.

**The Molecular Structure of Carbon Oxysulphide and Carbon Disulphide.** A. O. Rankine (*Phil. Mag.*, 1922, [vi], **44**, 292—300).—The mean collision areas of molecules of carbon oxysulphide and carbon disulphide are calculated from certain assumptions based on the Lewis-Langmuir theory of valency (cf. A., 1921, ii, 192, 584). The electronic configuration in carbon oxysulphide is the same as that of an arrangement of argon and neon atoms in the sequence neon–neon–argon, and that of carbon disulphide corresponds with the sequence of inert atoms argon–neon–argon. The radii of the outer electron shells of atoms possessing the electronic configurations of neon and argon are 0·65 Å. and 1·03 Å., respectively, and the radii of the collision spheres of argon and neon atoms are 1·15 Å. and 1·44 Å., respectively. For the purpose of intermolecular encounters, the molecules consist of overlapping spheres the centres of which are separated by 1·30 Å. for neon–neon and 1·68 Å. for the argon–neon combination, and of which the radii are the collision radii of argon and neon atoms. The mean collision area of carbon oxysulphide should lie between the limits $1·00\times10^{-15}$ cm.$^2$ and $1·09\times10^{-15}$ cm.$^2$ and of carbon disulphide between the limits $1·23\times10^{-15}$ cm.$^2$ and $1·37\times10^{-15}$ cm.$^2$. In the former case, the agreement between the results of this examination and the value obtained by Smith (cf. this vol., ii, 686) is striking. In the latter case, comparison is not yet possible. W. E. G.

**Valency Theories of Organic Chemistry.** F. Henrich (*Jahrb. Radioaktiv. Elektronik.*, 1922, **19**, 1—38).—An historical account of the theory of valency leading up to a discussion of modern views of Kossel, Hinsberg, J. Stark, Pauli, and Vorländer alone valency of organic compounds. W. E. G.

**The Electron Theory of Valency as Applied to Organic ompounds.** JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1922, , 1833—1834).—An addendum to a previous communication his vol., ii, 560).

The rupture of the union of two carbon atoms by oxidation, volving the loss of two electrons by one of the atoms or jointly both, takes place with particular ease when two neighbouring rbonyl groups are present in the molecule. In this case, there e no exposed valencies, but the structure is undoubtedly highly lar. *Thus oxalic acid may be formulated,*  , d the high polarity of the field surrounding the carbon atoms idently loosens the union between the two and exposes the ectrons held by them somewhat in the same manner, but not the same extent, as in the case of actual ionisation in a similar ld. Similar considerations are applied to cyanogen and to carbonyl derivatives in general. H. W.

**Lecture-room Demonstration of Atomic Models.** LOUIS . KING (*Phil. Mag.*, 1922, [vi], **44**, 395—400).—Atomic models e described in which a number of steel spheres or soft iron rods e arranged in a strong alternating magnetic field. A simple rm of the model consists of a coil of copper wire carrying alter- ting current over which is placed a large watch glass. Steel aring-balls are used as magnetic elements. Since the spheres pel each other with a force varying as the inverse fourth power the distance and the attraction to the centre varies as the stance, symmetrical stable groupings of the spheres are formed. hen two coils are employed, mercury is used as a floating surface r the steel balls. The system of spheres may be set in oscillation external magnets, giving a good illustration of the internal brations in the atom. The motion of molecules of a gas or the rownian movement may be illustrated by employing short linders of iron or steel wire, which undergo violent movements the field is suddenly applied. An experimental model illustrating e Rutherford atom may be constructed with two coils. Lengths steel wire placed axially to the coils are used to make up the icleus. Arrangements suitable for the demonstration of hydrogen helium atoms are described. W. E. G.

**Technical Sedimentation Analysis. I.** FRIEDRICH-VINCENZ N HAHN and DOROTHEA VON HAHN (*Kolloid Z.*, 1922, **31**, 96— 1).—The authors describe an apparatus, which is a slight odification of Ostwald and Hahn's two-limbed coagulation easurer, by means of which a rapid and accurate knowledge of e size of particles of commercial powders may be obtained. This paratus has been employed to determine the relative size of the rticles of a number of commercial preparations of soot and lamp- ack. As a control of the results obtained with this apparatus, e older methods of differentiation have also been used, and it shown that exactly similar results are obtained by all methods,

but that the new method is handier, more rapid, and more accurate (*cf.* this vol., ii, 205). J. F. S.

**Gas Generator with Washing Apparatus.** ROBERT MÜLLER, KOMANDIT-GESELLSCHAFT (D.R.-P. 346325; from *Chem. Zentr.*, 1922, ii, 978).—The apparatus consists of a conical flask fitted with a stopper which contains the essential features of the device. This consists of a tube, furnished with a funnel at the upper end and terminating in a trap at the lower end, through which the liquid used in generating the gas is introduced. The gas after generation passes through a washing apparatus of annular cross section fixed concentrically with the upper part of the tube.
G. W. R.

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## Inorganic Chemistry.

**Solubility of Sulphur in certain Organic Liquids.** R. DELAPLACE (*J. Pharm. Chim.*, 1922, [vii], **26**, 139—140).—The solubility of sulphur in chloroform, carbon tetrachloride, benzene, toluene, and ether was determined at various temperatures ranging from 13° to 24°. The divergence of the results from those obtained by earlier workers is attributed in some cases to the slowness of saturation, twelve hours' continuous agitation being necessary to obtain saturated solutions in toluene and benzene, for example. From the results, which are given in tabular form, the following figures for the weights of sulphur dissolved in 100 grams of solvent, are abstracted: in chloroform at 15°, 0·874 gram; in carbon tetrachloride at 15·5°, 0·645 gram; in toluene at 20°, 1·857 grams; in benzene at 15°, 1·582 grams; in anhydrous ether at 13°, 0·188 gram. G. F. M.

**Autoreduction of Sulphurous Acid.** GEORGE MACDONALD BENNETT (T., 1922, **121**, 1794—1795).

**Some Properties of Selenium Oxychloride. II.** VICTOR LENHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1664—1667; cf. A., 1921, ii, 256).—Selenium oxychloride is extremely hygroscopic and the very greatest precautions must be taken in preparing the anhydrous material. The presence of small quantities of water increases the electrical conductivity enormously, and its reactivity towards carbonates is largely dependent on the amount of water present. The best qualitative test for the presence of water in selenium oxychloride makes use of cobalt carbonate. When cobalt carbonate which has been dried at 200° for three hours is sealed up with anhydrous selenium oxychloride, *no action of any description* occurs, but if the merest trace of water is present the oxychloride becomes blue and if the tube is sealed a pressure of carbon dioxide is set up. The dry carbonates of calcium, strontium, copper, nickel, cobalt, and ferrous iron are unattacked by anhydrous

selenium oxychloride, whilst the dry carbonates of barium, lithium, and magnesium slowly evolve carbon dioxide and that of zinc much more rapidly. The fused carbonates of sodium and potassium react readily with anhydrous selenium oxychloride with the development of a large amount of heat. Sulphur dioxide is without action on boiling anhydrous selenium oxychloride, but in the presence of water selenium is precipitated. Dry hydrogen sulphide in contact with selenium oxychloride produces a reddish-brown colour, after which hydrogen chloride is evolved and yellow selenium sulphide produced. At the same time, heat is developed which dissociates the sulphide into sulphur and red seleninm. Liquid hydrogen disulphide reacts vigorously with selenium oxychloride in the cold, producing the same products as hydrogen sulphide. Carbon monoxide has no action on selenium oxychloride. Iodic acid, iodine pentoxide, and potassium iodate with selenium oxychloride give at first chlorine and then iodine chloride. Periodic acid with the oxychloride evolves chlorine and, when warmed, iodine chloride. Potassium bromate with selenium oxychloride in the cold gives chlorine followed rapidly by a mixture of bromine and chlorine. Selenium oxychloride warmed with potassium persulphate evolves chlorine, but in the presence of sulphuric acid the evolution occurs in the cold and with effervescence. Telluric and selenic acids evolve chlorine when gently warmed with the oxychloride. The metals tungsten, tantalum, and titanium are only slightly attacked hy selenium oxychloride after long treatment at high temperatures. Phosphorus reacts with selenium oxychloride at low temperatures to form phosphoric oxide, selenium monochloride, and selenium tetrachloride. Selenium oxychloride dissolves readily in carbon tetrachloride, but after a time reaction takes place with the formation of selenium tetrachloride and carbonyl chloride. Gliadin, zein, glutenin, elastin, and albumin are readily attacked and dissolved by selenium oxychloride. J. F. S.

**Selenium Oxybromide.** VICTOR LENHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1668—1673).—Selenium oxybromide is best prepared by adding to pure sublimed selenium dioxide the calculated amount of fused selenium in a flask fitted with a rubber stopper through which passes a dropping funnel and a safety tube filled with fused calcium bromide. The flask is cooled to 0° and the amount of bromine necessary to convert the metal into tetrabromide cautiously added in small quantities. The mixture is then warmed until the whole of the oxide has dissolved to form the oxybromide. Selenium oxybromide is a reddish-yellow solid, m. p. 41·5—41·7°, b. p. 217°/740 mm. with considerable decomposition, $d^{50}$ 3·38. The product decomposes so readily on heating, that it cannot be purified by distillation even under reduced pressure. It has an electrical conductivity at 40—50° of $6\times10^{-5}$ ohms$^{-1}$. Water converts it slowly into selenious and hydrochloric acids. It dissolves in carbon disulphide, chloroform, benzene, toluene, and xylene, and the fused material is miscible in all proportions with these solvents. Carbon tetrachloride dissolves it readily, but the

fused material dissolves only to the extent of 6%, and on heating the solution for several days carbonyl chloride is evolved and selenium tetrabromide formed. Selenium oxybromide is a very active chemical reagent. Sulphur reacts readily with it in the cold with the evolution of sulphur dioxide; selenium dissolves in it to form the monobromide. Yellow phosphorus explodes with the solid, whilst red phosphorus takes fire with the solid and burns. Iodine dissolves in large quantities in selenium oxybromide, whilst chlorine displaces bromine. Silicon and carbon are not attacked. Sodium reacts explosively with the oxybromide, producing the bromide and selenium monobromide, whilst potassium reacts even more violently. Mercury, arsenic, antimony, tin, bismuth, iron, calcium, copper, lead, silver, molybdenum, thallium, gold, platinum, and zinc are all attacked, forming the metallic bromide and selenium monobromide. Zinc dust burns in the oxybromide; aluminium and magnesium are only slightly corroded after heating for a week at 100° in the oxybromide. Cadmium, chromium, nickel, cobalt, tungsten, and tantalum are not attacked when heated for ten days at 100°. The oxides of mercury, silver, calcium, and sodium react energetically with selenium oxybromide, those of arsenic, tin, and tellurium less energetically, and those of columbium, tantalum, vanadium, thorium, titanium, zirconium, and uranium are unattacked after heating for several days at 100°. With most carbonates, the anhydrous oxybromide reacts only sluggishly even on heating, but in the presence of moisture the reaction is vigorous. The commoner sulphides react with the oxybromide with the development of heat, forming metallic bromides and selenium monobromide. Potassium chlorate liberates bromine from the oxybromide, but potassium perchlorate, permanganate, dichromate, and chromium trioxide are without action on it. When dry air is bubbled through the oxybromide at 60°, bromine is set free, due to a primary dissociation into the dioxide and tetrabromide followed by a secondary dissociation of the tetrabromide into bromine and the monobromide. Sulphur dioxide and carbon monoxide are without action on the oxybromide, and hydrogen sulphide causes a slight decomposition. J. F. S.

**Production of Colourless Glass in Tank Furnaces with Particular Reference to the Use of Selenium.** I. A. Cousen and W. E. S. Turner (*J. Soc. Glass Technology*, 1922, **6**, 168—181).—Numerous small melts at 1380° and 1440° showed that not more than 0·09% of iron oxide in a glass could be effectively decolorised by selenium or sodium selenite. The greater corrosive action of the salt-cake on the pot and its action on the selenium at high temperatures rendered more decoloriser necessary for batches containing this ingredient than for those with soda ash alone. Experiments showed the distinct formation of sodium selenite from selenium when dropped on to fused sodium sulphate. [illegible] batch containing only soda ash and no salt-cake, sodium selenite is much more effective than selenium in decolorising. Reheating [illegible]glasses only changed the tint of those which had been

over-decolorised, and then only when heated between 525° and 550°. A. C.

**Limits for the Propagation of Flame at Various Temperatures in Mixtures of Ammonia with Air and Oxygen.** ALBERT GREVILLE WHITE (T., 1922, **121**, 1688—1695).

**Acetone in Commercial Ammonia.** J. BOUGAULT and R. GROS (*J. Pharm. Chim.*, 1922, **26**, 170—171).—In many cases in which ammonia is used as a reagent in the presence of iodine, the formation of small quantities of iodoform is observed. An explanation of this fact was put forward by Guérin (A., 1909, i, 126), but this is set aside by the authors, who show that iodoform results from the presence of acetone. The quantity of acetone was found to vary from 0·01—0·5 gram per litre in the different samples examined, and it has been found in so-called "pure ammonia for analysis" in addition to the commercial product. It is pointed out that the use of ammonia in testing for acetone in physiological products is liable to give misleading results. H. J. E.

**Viscous Properties and Molecular Dimensions of Silicane.** A. O. RANKINE and C. J. SMITH (*Proc. Physical Soc.*, 1922, **34**, 181—186).—The authors have determined experimentally the viscosity of gaseous silicon hydride at 15° and 100°, and on the assumption that Sutherland's law holds for this gas over the whole temperature range concerned the viscosity at 0° has been extrapolated. The data have been used to calculate the mean collision area presented by the silicon hydride molecule in the gaseous state. The experimental method employed was the same as that previously described (A., 1921, ii, 694). The following numerical data are recorded: viscosity in C.G.S. units $\times 10^{-4}$, 0°, 1·078; 15°, 1·134; 100°, 1·436; Sutherland's constant, ($c$), 229; mean collision area of the molecule, ($A$), $0·989 \times 10^{-14}$ cm.$^2$. Using these data, an attempt is made to determine the structure of the silicon hydride molecule in relation to those of other gaseous hydrides the molecules of which have equal numbers of extra-nuclear electrons. J. F. S.

**Effect of Magnesia on the Resistance of Glass to Corroding Agents and a Comparison of the Durability of Lime and Magnesia Glasses.** VIOLET DIMBLEBY, CONSTANCE M. M. MUIRHEAD, and W. E. S. TURNER (*J. Soc. Glass Technology*, 1922, **6**, 101—107).—Magnesia glasses appear to possess a slight advantage over lime glasses as regards corrosion by water; they show no advantage in the case of hydrochloric acid, and are decidedly inferior as regards their resistance towards alkaline solutions. W. P. S.

**Crystal Structure of Potassium.** L. W. MCKEEHAN (*Proc. Nat. Acad. Sci.*, 1922, **8**, 254—255).—Determination by the X-ray method of the crystalline structure of potassium cooled to −150° in a current of air shows that the atoms of the metal are arranged in a body-centred cubic lattice with $a = 5·20 \times 10^{-8}$ cm. The

corresponding value of the density is 0·92 gram/cm.[3] compared with the commonly accepted value of 0·862 gram/cm.[3]. The difference is probably partly attributable to the imperfect crystallisation of samples previously examined. The observed crystalline structure does not persist as the temperature rises to about 20°.
J. S. G. T.

**Symmetry and Crystal Structure of Sodium Hydrogen Acetate.** RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], 4, 193—198).—Cubes (*d* 1·402) having the composition $NaH(C_2H_3O_2)_2$ were obtained by the long digestion of fused sodium acetate, glacial acetic acid, and acetic anhydride. The *X*-ray analysis (reflexion spectra and Laue photographs) gives a unit cube of edge 15·98 Å.U. containing twenty-four chemical molecules. The space group is probably $T_h^7$. L. J. S.

**Symmetry and Crystal Structure of Zinc Bromate Hexahydrate.** RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], 4, 188—192).—Good crystals having the composition $Zn(BrO_3)_2,6H_2O$, mostly octahedral in habit, are formed by the slow cooling, or slow evaporation, of solutions. Reflexion *X*-ray photographs were obtained from the octahedral face, and Laue photographs through both octahedral and cube faces. These show an absence of planes of symmetry. From the various alternative arrangements, the space group $T_h^6$ is selected. The unit cube contains four chemical molecules and has length of edge 10·31 Å.U. L. J. S.

**Chemical Method of Separating the Isotopes of Lead.** THOMAS DILLON, ROSALIND CLARKE, and VICTOR M. HINCHY (*Sci. Proc. Royal Dublin Soc.*, 1922, 17, 53—57).—The authors have attempted to effect a separation of the isotopes of lead by means of the Grignard reaction. Lead chloride prepared from some residues recovered from the manufacture of mesothorium was treated with lead tetraethyl and the reaction represented by the equation $2PbCl_2+4MgRX=R_4Pb+2MgCl_2+2MgX_2+Pb$ carried out. The lead tetraethyl and metallic lead remaining *constitute two fractions which are used separately in a repetition* of the process. The process was carried out twice and the atomic weight of the lead in the tetraethyl from one and the lead residue in the other process was then determined by the method employed by Soddy and Hyman (T., 1914, 105, 1402). The relative values 207·1 and 207·4 were obtained, thus indicating that the above reaction furnishes a possible method of separating isotopes and that the chemical properties of isotopes although similar are not identical. J. F. S.

**The Mass-spectrum of Iron.** F. W. ASTON (*Nature*, 1922, 110, 312—313).—The mass spectrum of iron, examined as iron pentacarbonyl mixed with carbon dioxide, is characterised by a strong line at 55·94±0·05, and possibly a very faint line at 54. nickel A. A. E.

**The Constitutional Diagram of the Iron–Carbon System based on Recent Investigations.** Kôtarô Honda (*Sci. Rep. Tohoku Imp. Univ.*, 1921, **11**, 119—129).—In a previous communication with Murakami (cf. A., 1921, ii, 699), it is shown that the graphitisation of iron always takes place after solidification of the fusion, the formation of graphite being due to the catalytic action of carbon monoxide on the solid cementite, just below the eutectic point, 1130° to 1100°. This being the case, the graphite lines on the usual double iron–carbon diagrams must be omitted. The shape of the solidus curve is frequently given incorrectly; according to the principles of thermodynamics, this curve, like the liquidus curve, should be bent upwards. In a discussion of the allotropic transformations of the various forms of iron, it is concluded that the $\alpha$—$\beta$ transformation is not a sudden change of phase, but a progressive change beginning from the lowest temperatures and ending at about 790°, the amount of change being dependent on tho temperature. The magnetisation of iron is not accompanied by changes in the atomic configuration as in the case of allotropic change, but is a consequence of a gradual alteration in the energy of the atoms with rise in temperature. This transformation is represented by a dotted line passing through 790° for pure iron and 775° at 4% of carbon. Similarly, the cementite transformation is progressive and extends from the lowest temperature up to 215°. The break in the heating curve of cast iron observed by Ruer (A., 1921, ii, 198) is not evidence of the existence of a graphite eutectoid. W. E. G.

**Crystal Structure of Iron and Steel. II.** Arne Westgren and Gösta Phragmén (*Z. physikal. Chem.*, 1922, **102**, 1—25; cf. this vol., ii, 152).—Röntgen photographs of iron wire at 800°, 1100°, and 1425°, obtained by the Debye and Scheerer method, show that iron within the so-called $\beta$ and $\delta$ regions similarly to $\alpha$-iron has a space-centred cubic lattice, whilst iron in the $\gamma$-iron region has a face-centred cubic lattice. The characteristic fact is therefore that the transition which occurs at 900° ($A_3$) is reversed at 1400° ($A_4$). The $\gamma$-iron lattice of austenite steel is extended by the dissolved carbon. It is found that a steel containing 1·98% of carbon possesses a larger iron lattice when it is quenched at 1100° than at 1000°, also that the $\alpha$-iron lattice in martensite appears to be somewhat extended by the carbon. The homogeneous lattice region within the $\alpha$-iron in martensite is shown to be extremely small. A steel containing 0·80% of carbon which has been quenched at 760° is shown to be practically amorphous. Debye photographs of cementite and spiegeleisen crystals are identical. By means of Laue photographs and an investigation of the interferences of a spiegeleisen crystal rotating in a Debye camera, it is shown that cementite belongs to the rhombic system and has an axial ratio 0·670 : 0·755 : 1. The dimensions of the elementary parallelopiped are 4·53, 5·11, and 6·77 Å.U., respectively. The unit crystal contains four molecules of $Fe_3C$, from which it follows that the specific gravity of cementite is 7·62.

**The System Chromium Trioxide–Sulphur Trioxide–Water.** LIONEL FELIX GILBERT, HAROLD BUCKLEY, and IRVINE MASSON (T., 1922, **121**, 1934—1938).

**Rôle of Chromates in Electrolysis for Chlorate.** A. V. PAMFILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 113—117).—Chromate plays a triple part in the electrolytic production of chlorate in an acid solution. (1) It acts as a "buffer" salt, regulating automatically the kinetic acidity of the liquid. (2) It forms a film on the cathode and thus prevents reduction of the hypochlorite formed as an intermediate product, and (3) this film protects the cathode from disintegration and hence allows the platinum electrodes to be replaced by those of metals more readily accessible, such as copper. These effects of chromate are specific and are not exhibited by any other compound. T. H. P.

**The Adsorption of Uranium-X and its Isotope, Thorium, by Basic Ferric Acetate.** ANDREW CHARLES BROWN (T., 1922, **121**, 1736—1743).

**Zirconium Ferrocyanide and Ferricyanide.** F. P. VENABLE and E. O. MOEHLMANN (*J. Amer. Chem. Soc.*, 1922, **44**, 1705—1707).—When solutions of potassium ferrocyanide are added to solutions of zirconyl salts, white precipitates are obtained which are unstable in the air and of varying composition. The precipitates are basic zirconium ferrocyanides and the composition depends on the extent to which the hydrolysis has proceeded. Thus, a freshly prepared solution of zirconyl chloride gives a substance of the formula $ZrO(OH)_2,(ZrO)_2Fe(CN)_6$ and a solution which has been boiled gives a precipitate of the composition $9ZrO(OH)_2,2(ZrO)_2Fe(CN)_6$. Potassium ferricyanide gives no precipitate with freshly prepared solutions of zirconyl chloride, but on boiling the mixture the very basic compound

$$21ZrO(OH)_2,2(ZrO)_3Fe(CN)_6$$

is precipitated. J. F. S.

**The Chemical Properties of Mesothorium. II.** D. YOVANOVITCH (*Compt. rend.*, 1922, **175**, 307—309).—A concentrated solution of the chlorides of barium and radioactive elements was treated with hydrochloric acid in the cold. The precipitated barium chloride carried down with it mesothorium-*I*, thorium-*X*, and radium, leaving mesothorium-*II*, radiothorium, and the active residue in solution. By this process, repeated at intervals, mesothorium-*II* was obtained in the acid solution, nearly pure and practically free from barium. The final purification of mesothorium-*II* was carried out by repeated co-precipitation with salts of iron or aluminium, and further by reprecipitation as hydroxide. To eliminate radiothorium a trace of thorium was [illegible]ded and later removed by means of hydrogen peroxide. [illegible]orium-*C* and thorium-*B* were removed by precipitation with [illegible]ta and bismuth, which in turn were removed as sulphides. [illegible]horium-*II* in solution with elements of the cerium group was [illegible]ally precipitated as oxalate hydroxide, and as the double

sulphate. Mesothorium-*II* in the presence of lanthanum and praseodymium appeared in greater quantity in the early fractions, but when mixed with neodymium and samarium was more concentrated in the last fractions. In the fractionation of the double nitrates of the rare earths and ammonium, mesothorium-*II* tends to accumulate with lanthanum rather than with samarium.

A. G. P.

**Crystal Structure of Germanium.** N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 125—126).—In continuation of previous work (A., 1921, ii, 200), the author has investigated the crystal structure of germanium, by the powder method. The structure, deduced from the observations, resembles that of the diamond, the lattice parameter *a* being equal to 5·61 Å., compared with the value 5·594 Å. deduced from the value of the density and atomic weight, taking Avogadro's number equal to $6 \cdot 062 \times 10^{23}$. As modifications of carbon, silicon, germanium, and tin resembling the diamond in structure are known, whilst the same is not true of titanium, zirconium, and thorium, it is concluded that carbon and silicon are more closely associated with the elements of group IV*b* than with those of group IV*a*.

J. S. G. T.

**The Anode Oxidation of Gold. I. Anode Oxidation of Gold in Sulphuric Acid.** FR. JIRSA and OT. BURYÁNEK (*Chem. Listy*, 1922, **16**, 189—194).—A detailed examination is made of the oxidation of a gold anode in dilute sulphuric acid. The product obtained is shown to be auric hydroxide, which loses a molecule of water on keeping over phosphoric oxide, giving the compound AuO(OH), and this, on further dehydration, yields the oxide $Au_2O_3$. It was observed that ozone is evolved during the passage of the current, and the amount produced per ampere-hour for various concentrations of acid is determined. The yields of hydroxide obtained with different currents and acid concentrations are also measured.

The solubilities of auric hydroxide, both freshly prepared and stale, and prepared both electrolytically and by hydrolysis, are determined for different concentrations of sulphuric acid, and from these results it is concluded that the product of solution is auric sulphate, and not the compound $Au(OH)SO_4$.

R. T.

## Mineralogical Chemistry.

**The Composition and Calorific Power of Coal from the Deeper Strata of the Kenadza (Algerian) Mine.** A. FOUX (*Bull. Soc. chim.*, 1922, [iv], **31**, 813—816).—Coal from the deeper workings differs from that obtained nearer the surface by reason of its greater proportion of ash, nitrogen, and sulphur. The heat of combustion is about 8·255 calories per gram.

H. J. E.

**Colloidal Phosphates.** CARL ELSCHNER (*Kolloid Z.*, 1922, **31**, 94—96).—The author describes the colloidal formation of a clay found in the Fanning Islands which contains no silicates but is chiefly made up of calcium phosphates and organic materials. The mineral *naurite* is stated to be formed from a jelly-like mass containing tricalcium phosphate with uric acid and purine derivatives, which through the action of nitrifying bacteria has lost its organic matter and formed a substance of the composition $3(Ca_3P_2O_8),Ca(OH)_2,xH_2O$. Another mineral, *meyersite*, found in the Hawaii Islands, is described. This is an aged gel of the composition $AlPO_4$, 66·33%; $FePO_4$, 2·52%; $H_2O$, 26·10%; and is to be distinguished from variszite, $AlPO_4,2H_2O$. It is lighter in colour and is particularly characterised by its banded structure. The mineral is formed by the decomposition of lava by the constituents of guano. J. F. S.

**Olivine from Lithosiderites.** P. CHIRVINSKII (*Bull. Soc. franç. Min.*, 1921, **44**, 170).—Olivine isolated from the pallasites of: I, Ahumada; II, Finmarken (*d* 3·366); III, Mt. Dyrring; and IV, Molong, gave:

| | $SiO_2$. | FeO. | MnO. | MgO. | CaO. | Total. |
|---|---|---|---|---|---|---|
| I. | 38·43 | 14·93 | trace | 46·27 | 0·40 | 100·03 |
| II. | 39·32 | 16·61 | — | 44·07 | — | 100·00 |
| III. | 40·52 | 13·13 | — | 47·30 | trace | 100·95 |
| IV. | 39·32 | 13·13 | trace | 47·70 | trace | 100·15 |

L. J. S.

**Cyprine and Associated Minerals from Franklin, New Jersey.** J. VOLNEY LEWIS and LAWSON H. BAUER (*Amer. J. Sci.*, 1922, [v], **4**, 249—251).—Sky-blue, granular to fibrous cyprine (a variety of idocrase), which was apparently homogeneous, was found on microscopical examination of thin sections to enclose about 33% of rounded grains of willemite. Analysis I gives, after deducting willemite, the figures under II agreeing approximately with the composition of idocrase. Associated with this mineral is pale pink, cleavable to coarsely fibrous rhodonite (var. bustamite), which gave analysis III; brown, granular garnet—the polyadelphite variety of andradite (analysis IV); also phlogopite, felspar, etc.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | ZnO. |
|---|---|---|---|---|---|---|
| I. | 32·42 | 14·07 | — | 0·77 | 1·50 | 21·71 |
| II. | 35·14 | 20·86 | — | — | — | — |
| III. | 46·72 | 1·34 | — | 0·46 | 26·51 | 1·34 |
| IV. | 34·28 | 3·12 | 25·53 | — | 7·41 | — |

| | CuO. | CaO. | MgO. | $H_2O$. | Total. |
|---|---|---|---|---|---|
| I. | 0·99 | 25·22 | 1·08 | 2·38 | 100·14 |
| II. | 1·47 | 37·40 | 1·60 | 3·53 | 100·00 |
| III. | — | 22·24 | 1·27 | — | 99·88 |
| IV. | — | 29·20 | 0·39 | — | 99·93 |

## Analytical Chemistry.

**Refractometric and Interferometric Quantitative Analysis.** J. Bečka (*Z. physiol. Chem.*, 1922, **121**, 288—299).—The author has extended the observations of de Crinis (A., 1920, ii, 700) on the use of the refractometer for the analysis of solutions so as to make it more generally applicable. He has also described the use of the interferometer for more dilute solutions. The experiments have special reference to urine analysis. H. K.

**Recovery of Solvents from Extracted Substances.** A. B. Pichler (*Chem. Ztg.*, 1922, **46**, 698).—In the ordinary method of extracting substances in a Soxhlet apparatus a considerable quantity of the solvent is retained by the extraction thimble and its contents, particularly if the latter are of a bulky nature; this solvent may be recovered by transferring the thimble, at the end of the extraction, to a large flask and, when a suitable number of thimbles have thus been collected, submitting them to distillation. To recover solvent from a single thimble, the latter may be transferred to a tube which fits on to the lower end of the Soxhlet apparatus and the solvent then distilled into and collected in the Soxhlet apparatus.
W. P. S.

**Apparatus for Measuring the Hydrogen-ion Concentration of a Solution.** André Kling and A. Lassieur (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 232—238).—A further description of the electrometric method previously reported (this vol., ii, 234). G. F. M.

**Colorimetric Estimation of Hydrogen Peroxide.** M. L. Isaacs (*J. Amer. Chem. Soc.*, 1922, **44**, 1662—1663).—A rapid method of estimating the concentration of hydrogen peroxide colorimetrically based on the method described by Denigès (A., 1890, 1185) and Crismer (A., 1892, 381) is worked out and fully described. About 30 c.c. of water, 10 c.c. of a 5% solution of citric acid, and 1 c.c. of the unknown hydrogen peroxide are placed in a 50 c.c. graduated flask and, after mixing, 1 c.c. of a 10% solution of ammonium molybdate is slowly added. Water is then added to make the volume 50 c.c. and the whole well shaken. The yellow colour develops at once and the solution is then compared with a standard potassium chromate solution (0·4 gram/litre) in a Dubosq colorimeter. When the standard is set at 20 the quantity of hydrogen peroxide is given by $x=0{\cdot}05467/y$, where $y$ is the colorimeter reading and $x$ the number of grams of peroxide in the 50 c.c. of solution. The results obtained by this method compare extremely favourably with those obtained by direct titration with potassium permanganate. J. F. S.

**The Error in Estimating Chloride by Bang's Micro-Method.** Richard Priggoe (*Biochem. Z.*, 1922, **130**, 442—447).—The sources of error in this method have been examined

and full details of the technique required for the greatest exactitude are given. H. K.

**Micro-analyses by Bang's Methods. I.** LUDWIG PETSCHACHER (*Biochem. Z.*, 1922, **131**, 116—123).—The estimation of chlorides by microanalysis in drops of blood gives sufficiently accurate results, but the estimation of dextrose and residual nitrogen is not sufficiently accurate. H. K.

**Colorimetric Estimation of Blood Chlorides.** M. L. ISAACS (*J. Biol. Chem.*, 1922, **53**, 17—19).—The method is applicable to the tungstic acid blood filtrates and depends on the conversion of silver chromate into sodium chromate by the action of the blood chlorides. Excess of silver chromate (about 0·05 gram) is stirred into 10 c.c. of the blood filtrate previously neutralised by addition of a small quantity of magnesium carbonate. After centrifuging, the supernatant liquid (plus washings) is clarified by the addition of 1 c.c. of a 2% ammonium hydroxide solution, and diluted to 25 c.c. The colour is then compared with a potassium chromate solution which has been standardised by means of a solution of sodium chloride in the above manner. E. S.

**Estimation of Chlorine in Tissues.** O. M. PICO and J. MURTAGH (*Compt. rend. Soc. Biol.*, 1922, **86**, 405—406; from *Chem. Zentr.*, 1922, ii, 922).—The tissue is dissolved in concentrated sodium hydroxide solution and the proteins are precipitated by phosphotungstic acid. The chlorine is estimated in the filtrate by the method of Austin and Van Slyke. G. W. R.

***Detection of Iodates in Potassium Iodide according to the French Codex, 1908.*** LACHARTRE (*J. Pharm. Chim.*, 1922, [vii], **26**, 134—138).—The test for iodates in potassium iodide described in the Codex lacks precision, and takes no account of the influence of such factors as the strength of the iodide solution, the amount of acid added, the duration of the reaction, etc. The following method is suggested. A 10% solution of the iodide in distilled water is prepared, and to 10 c.c., 3 c.c. of chloroform and 5 drops of glacial acetic acid are added. After shaking for thirty seconds, the chloroform, examined immediately after separation, should not be coloured. Performed in this manner, the limit of sensitiveness of the test is 0·08 part of iodate per 1000, which is considered to be all that is required for a reasonably pure product. The presence of copper in small quantities, for example, 0·0015 part per 1000, has no effect on the reaction with a perfectly pure iodide, but it appreciably accelerates the development of the iodine coloration when traces of iodate are present. The amount of copper in ordinary distilled water is, however, too small to have any effect on the reaction in either case. G. F. M.

**Detection and Estimation of Fluorides.** N. K. SMITT (*Bull. Bureau Biotech.*, 1922, 176—178).—Greeff's volumetric method for the estimation of fluorides (A., 1913, ii, 975) may be simplified somewhat by the use of an alcoholic solution of ferric chloride. The presence of fluoride in neutral solution may be detected by

adding a little ammonium thiocyanate solution and then ferric chloride solution drop by drop; in the absence of interfering substances, rapid disappearance of the colour of the ferric thiocyanate indicates the presence of fluoride. Even insoluble fluorides, such as that of calcium, may be similarly detected if the substance is vigorously ground in a mortar with thiocyanate and ferric chloride solutions. A colorimetric method for estimating traces of fluorides, based on the above reaction, is also described. [Cf. *J. Soc. Chem. Ind.*, 1922, Oct.] T. H. P.

**The Estimation of Oxygen in Organic Compounds.** H. TER MEULEN (*Rec. trav. chim.*, 1922, **41**, 509—514; cf. Boswell, A., 1913, ii, 334).—The substance to be analysed is heated in a current of pure hydrogen and the resulting gases are passed first over metallic nickel in the form of thin wire and secondly over nickelised asbestos. The function of the former is that of transforming the decomposition products of the substance into compounds which are suitable for hydrogenation, which reaction occurs in the presence of the latter. With proper precautions, all the oxygen is transformed into water and weighed as such; but as a portion may remain as carbon dioxide, a second absorbent is required to obviate error due to incomplete transformation. Analyses carried out by this method have yielded satisfactory results, details of which are given. Halogens and sulphur act as poisons to the catalyst; the method is therefore not applicable to substances containing these elements. As calcium chloride is used to absorb the water formed in the reaction, nitrogenous substances may not be dealt with by this method on account of the ammonia which they yield on hydrogenation. H. J. E.

**Estimation of Sulphides by Oxidation by means of Ferric Sulphate.** P. P. BUDNIKOV and K. E. KRAUZE (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 157—159).—The method described is based on the reactions $3Na_2S+Fe_2(SO_4)_3=3Na_2SO_4+2FeS+S$ and $2FeS+2Fe_2(SO_4)_3=6FeSO_4+2S$, the ferrous sulphate thus formed being estimated by titration with permanganate solution. If the ferric sulphate is used in aqueous solution, it undergoes hydrolysis, whereas in presence of acid the sodium sulphide may be attacked with loss of hydrogen sulphide. These difficulties are avoided by adding sodium carbonate or hydroxide, and by acidifying, only after the oxidation, with phosphoric acid. Manganous sulphate is added prior to the titration. The method is applicable to calcium and zinc sulphides, but not to sulphides of copper, lead, silver, etc., which are insoluble. T. H. P.

**Estimation of Non-protein Nitrogen by means of Ultrafiltration.** M. RICHTER-QUITTNER and H. HOENLINGER (*Wiener Klin. Wochschr.*, 1921, **34**, 24).—Twenty c.c. of blood plasma or serum are diluted ten to twenty times with distilled water and filtered through a Buchner funnel and membrane (Zsigmondy and Jander, A., 1919, ii, 520), the non-protein nitrogen being estimated in the filtrate by Kjeldahl's or Pregl's micro-method.

CHEMICAL ABSTRACTS.

**The Triketohydrindene (Ninhydrin) Reaction as a Quantit ative Colorimetric Method for the Estimation of Amino acid Nitrogen.** H. Riffart (*Biochem. Z.*, 1922, **131**, 78–96).—The ninhydrin reaction is suitable for the estimation o amino-acid nitrogen if certain precautions are taken. All th amino-acids with free amino-groups examined, except histidine give at $P_H$ 6·976 the same standard colour if the solutions be equa in amino-acid nitrogen content, say, 10 mg. or less per litre. Thi result is obtained by taking 2 c.c. of such a solution, neutralisin with $N$/400 alkali to $P_H$ 6·976 by comparison with phosphat standards and methyl-red, adding 2 c.c. of phosphate solution o the same $P_H$ and 1 c.c. of 1% ninhydrin solution, and heatin for thirty minutes in the boiling-water-bath. The solutions ar then diluted to 100 c.c. and estimated colorimetrically. Histidin gives the standard colour at $P_H$ 6·24, thus involving a small erro where mixtures of amino-acids contain this acid. Some amine and ammonium salts also give the colour reaction, but only in concentrations higher than 15 mg. per litre. H. K.

**Estimation of Phosphorus in Minerals and in Coke Ash by a Colorimetric Method.** Georges Misson (*Bull. Soc. Chim. Belg.*, 1922, **31**, 222—225).—The phosphorus to be estimated is obtained in solution as phosphate, and it is essential that the solution should be free from chlorine. Potassium permanganate is added, followed by a solution of sodium peroxide in dilute nitric acid. After addition of ammonium vanadate, the solution is boiled and treatment with ammonium molybdate produces the colour which is compared with the standard tint. Three modifications of the method are given, (*a*) for minerals of small phosphorus content, 0·01—0·20%; (*b*) for minerals of greater phosphorus content, 0·20—2·50%; (*c*) for coke ash, together with details of the procedure in each case. A comparison of the results with those obtained by gravimetric methods shows that they are substantially in agreement, but the colorimetric method gives somewhat lower results for a phosphorus content of 1·7% and upwards.

H. J. E.

**Modification of the Bell-Doisy Phosphate Method.** A. P. Briggs (*J. Biol. Chem.*, 1922, **53**, 13—16; cf. A., 1920, ii, 769).—In the modification described, the coloration produced in acid solution, which is more stable than that in alkaline solution, is used for the estimation. The blood or plasma is diluted with 3 volumes of water and 1 volume of 20% trichloroacetic acid, shaken vigorously for a few seconds, and filtered after ten minutes. To 5 c.c. of the filtrate (corresponding with 1 c.c. of plasma), 2 c.c. of the molybdate solution, 1 c.c. of a 20% sodium sulphite solution, 1 c.c. of the quinol solution, and water to bring the volume to 10 c.c. are added. After thirty minutes, the coloration produced is compared with a standard. In the presence of the sodium sulphite reagent a blue coloration is obtained which is more intense than the green coloration produced in its absence. The method is applicable to urine.

**Estimation of Lipoid Phosphoric Acid ("Lecithin") in Blood by Application of Bell and Doisy's Method for Phosphorus.** F. S. RANDLES and ARTHUR KNUDSON (*J. Biol. Chem.*, 1922, **53**, 53—59).—An alcohol–ether extract of blood or plasma is prepared according to Bloor's procedure (A., 1918, ii, 452). An aliquot part of this is evaporated, treated with sulphuric and nitric acids, and heated until the latter acid is completely driven off. Phosphoric acid is then estimated in the clear solution by Bell and Doisy's method (A., 1920, ii, 769). Disturbance of the final solutions produces bubbles which interfere with the reading. The solutions should therefore be left in the colorimeter cups for five minutes before making the comparison. E. S.

**Conductometric Titration of Hydrofluosilicic Acid.** NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 556—560).—Using two adjustable parallel platinum plates as electrodes, the author has carried out the conductometric titration of hydrofluosilicic acid. When a mixture of 100 c.c. of water and 170—200 c.c. of 95% alcohol was used as solvent for the 0·138*N*-acid, the titration was conducted with sodium hydroxide solution as well as with potassium hydroxide solution without causing hydrolysis of the acid. K. K.

**Critical Examination of Methods commonly used in Determining the Durability of Glass.** W. E. S. TURNER (*J. Soc. Glass Technology*, 1922, **6**, 30—45).—The methods investigated involved (1) the testing of the surface of glass vessels, (2) the use of plates, disks, or slabs of glass, (3) the treatment of the glass in the form of powder, and (4) the autoclave test. Whilst there are uncertainties in the results obtained by any of the methods, it is not difficult to distinguish qualitatively a good glass from a poor one. It is suggested that, in absence of a satisfactory general test, the tests should be made on plates of the glass or on the powder, preferably the latter. W. P. S.

**New Apparatus for Estimation of Carbon Dioxide in Air.** HENRIK LUNDEGÅRDH (*Biochem. Z.*, 1922, **131**, 109—115).—The author has modified the Pettenkoffer method by replacing the flask by a zinc vessel in the form of a beaker with detachable cover, and fitted with three tubes to facilitate withdrawal and entry of solutions. A larger apparatus is also described on similar lines, suitable for use in the open. H. K.

**Estimation of Gases in Metals.** HAROLD LESTER SIMONS (*Chem. and Met. Eng.*, 1922, **27**, 248—249).—A weighed quantity of the metal is introduced into a specially designed apparatus which is then exhausted by means of a Toeppler pump. Mercury is allowed to siphon over into the flask containing the metal and the whole is heated until the latter dissolves. The evolved gases are first examined spectroscopically in a Geissler tube, then transferred to the usual gas apparatus, and the quantity of each constituent estimated in the usual manner. [Cf. *J. Soc. Chem. Ind.*,

**Estimation of Small Quantities of Sodium in Aluminium and Alumina.** R. GEITH (*Chem. Ztg.*, 1922, **46**, 745).—The precipitation of aluminium hydroxide by even a very slight excess of ammonia is invariably not quite complete and the traces in solution are weighed with the sodium chloride. By electrolysis of a nearly neutral solution of aluminium chloride or sulphate containing iron, magnesium, calcium, and sodium salts as impurities, all the sodium may be deposited in a mercury cathode as amalgam whilst the bulk of the other metals are precipitated as hydroxides in the solution and the chlorine escapes as gas from the carbon anode. In a suitably arranged divided cell the mercury is made the cathode in the inner compartment and the anode in the outer, which contains dilute neutral sodium chloride solution and a nickel rod dipping into the mercury and forming a voltaic couple. The sodium then redissolves as hydroxide in the salt solution and its amount may be estimated by titration. The current required for the method is 0·15 ampere at 3·5 volts for two to three hours. [*Cf. J. Soc. Chem. Ind.*, 1922, 714A.] A. R. P.

**A New Method of Qualitative Separation of the Alkaline-earth Metals.** MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 806—810).—The separation is based on the differences in solubility of the sulphites and thiosulphates of the three metals in ethyl alcohol–water mixtures. The carbonates as precipitated in the group are dissolved in acetic acid, and the solution is boiled and neutralised with ammonia. After addition of ethyl alcohol, the barium is precipitated by alcoholic sodium thiosulphate. A small proportion remains in solution; this is separated, after filtration, by addition of potassium sulphate, but not of sufficient concentration to precipitate any strontium. The strontium is then separated as sulphite by excess of alcoholic sodium sulphite or as sulphate by excess of potassium sulphate. The solution is then acidified with very dilute acetic acid and the calcium precipitated by ammonium oxalate. The concentrations of the reagents required to effect the separation are given, also the proportions in which they are to be used. H. J. E.

**Approximate Volumetric Estimation of Barium.** MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 810—813; cf. previous abstract).—The separation of barium from strontium and calcium as thiosulphate may be utilised as a means of volumetric estimation by using excess of a standard sodium thiosulphate solution which contains ethyl alcohol. After allowing the mixture to remain for twenty-four to thirty-six hours to obtain as complete a precipitation of barium thiosulphate as possible, the solution is filtered and the excess of the reagent estimated. The quantity of barium present is thus found by difference. A correction is necessary by reason of the slight solubility of barium thiosulphate; this is applied by a formula given by the author, as the temperature at which the precipitation takes place and the percentage of alcohol present are factors which influence the result. H. J. E.

**Use of Amalgams in Volumetric Analysis. V. Estimation of Iron, Titanium, Uranium, and Methylene-blue.** SUETARÔ KIKUCHI (*J. Chem. Soc. Japan*, 1922, **43**, 544—550; cf. A., 1921, ii, 596, 714; this vol., ii, 519, 529).—After the reduction of mixed solutions of two metals with liquid zinc- or cadmium-amalgam, their differential titration with two standard oxidising solutions was studied. A mixture of ferric oxide and titanium dioxide is titrated with potassium permanganate and iron alum, using ammonium thiocyanate as an indicator after reduction with zinc amalgam. They are quantitatively oxidised with iodine in the presence of sodium tartrate. Combining this reaction and that with iron alum, they can also be differentially titrated. A mixture of ferric oxide and uranium trioxide is titrated with potassium permanganate and iron alum, after reduction with cadmium amalgam in warm solution and in the presence of carbon dioxide. A mixture of titanium dioxide and uranium trioxide is titrated with potassium permanganate and iodine solutions, after reduction with cadmium amalgam in warm solution. Quadrivalent uranium is not oxidised by excess of iodine in the presence of sodium tartrate.

After a mixed solution has been oxidised with potassium permanganate, it is reduced with the amalgam and titrated differentially with iron alum or iodine. A definite quantity of titanic sulphate is reduced to tervalent titanium salt by the amalgam; methylene-blue is added at 60—70° until the solution is tinged with blue, and then it is titrated. The purity of Kahlbaum's methylene-blue B extra was 82·96%, and that of Merck's methylene-blue B.B, 85·07%. K. K.

**Use of Amalgams in Volumetric Analysis. VI. Electrometric Titration of Iron, Molybdenum, Uranium, Vanadium, and Titanium.** NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 550—556; cf. preceding abstract).—Solutions of iron alum, ammonium molybdate, uranyl sulphate, vanadic acid, and titanium sulphate are reduced with zinc amalgam, separated from the amalgam, connected to the platinum and calomel electrodes, and their *E.M.F.* estimated, the standard solution of potassium permanganate meanwhile being gradually added. In these estimations, the volumes of the solution should be maintained as small as possible. In the case of titanium, a slight deficiency of the permanganate solution is first added, then excess of iron alum solution to oxidise tervalent titanium, and the solution then titrated with the permanganate solution. A mixture of iron and titanium can be electrometrically titrated with the permanganate solution, two break-points in the *E.M.F.* curve showing the end points.

K. K.

**Estimation of Tin in Bearing Metals.** JOSEF NÁGEL (*Chem. Ztg.*, 1922, **46**, 698).—One gram of the metal turnings is dissolved by boiling in a flask with 100 c.c. of hydrochloric acid and 3 grams of potassium chlorate; after all free chlorine has been expelled, the solution is diluted with 30 c.c. of water, 7 grams of sodium chloride are added, and, after the addition of a strip of nickel having

an area of about 10 sq. cm., the solution is boiled for one hour. The stannic chloride is thus reduced to stannous chloride, whilst the antimony is deposited as flakes on the nickel plate. After the solution has been cooled in an atmosphere of carbon dioxide, the stannous chloride is titrated with standardised iodine solution.

W. P. S.

**The Volumetric Estimation of Antimony and Tin in Red Brass.** FRANZ JOHANN MÜCK (*Chem. Zig.*, 1922, **46**, 790).—The alloy is dissolved in nitric acid and the precipitated stannic and antimonic acids are collected, washed, and dissolved in hot sulphuric acid and potassium sulphate. The cooled solution is treated with 0·5 gram of tartaric acid, 180 c.c. of water, and 7 c.c. of hydrochloric acid and the antimony estimated by titration with permanganate. The solution is then boiled with a further 30 c.c. of water, 60 c.c. of hydrochloric acid, and 2—3 grams of metallic antimony, and the tin is estimated by titration with iodine [cf. *J. Soc. Chem. Ind.*, 1922, Oct.].

A. R. P.

**Decomposition and Analysis of Monazite.** P. WENGER and P. CHRISTIN (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 231—232).—The hitherto pnblished methods for the attack of monazite are either long and delicate, or else leave large quantities of the rare earths undissolved. By the following method the whole of the mineral can readily be brought into solution. Abont 1 gram of the finely ground material is heated for five hours with 5 c.c. of sulphuric acid (*d* 1·84) at 230°. The resulting pasty mass is gradually poured into iced water, when all but a small residue passes into solution. This residue is collected on a filter and again heated with sulphuric acid, a little hydrofluoric acid being added to volatilise the silica. The residue in the crucible is then melted with six parts of sodium carbonate. On addition of water, the tantalum passes into solution, and any slight residue which still may remain will be zirconia, which is rendered soluble by fusion with potassium hydrogen sulphate. In the subsequent analysis the precipitation of the rare earths by oxalic acid should be conducted at 55° in a solution containing 0·15—0·75% of sulphuric acid and with an excess of 3% of oxalic acid. At this temperature the precipitation may be considered quantitative for yttrium, thorium, cerium, and didymium. Lanthanum oxalate, being the most soluble, is not completely precipitated, and 50 c.c. of the solution under the above conditions would retain 0·0011 gram of lanthanum in solution.

G. F. M.

**The Use of Hanuš's Method for the Determination of the Iodine Figure of Mineral Oils.** JAN HLADKÝ (*Chem. Listy*, 1922, **16**, 207—211).—The method of Hanuš, whereby the iodine figure of mineral oils and bitumens is determined by means of a solution of iodine bromide in carbon tetrachloride, is examined. It is found that the reagent does not depreciate as rapidly as those preed in the methods of Hübl and of Wijs (E. Graefe, *Petroleum*, 1916, **12**, 631), and that the difference produced in the iodine

figure by increasing the time allowed for reaction is smaller than for the above methods. The concentration of the reagent, and the reaction temperature are not of great importance, whilst it is essential that the quantity of oil used is such as to leave a large excess of reagent after interaction. The presence of small quantities of water does not appear to affect the reaction. A further advantage of this method is that it permits the use of carbon tetrachloride, a universal solvent for the bitumens. The accuracy attainable is, for oils of a low iodine figure, from 1 to 2 units. R. T.

**The Iodine Values of Aliphatic and Aromatic Unsaturated Compounds.** D. HOLDE [with P. WERNER, IDA TACKE, and C. WILKE] (*Chem. Umschau*, 1922, **29**, 185—188).—In the case of oleic acid anhydride and erucic acid, the iodine values found by the Hanuš method or by the Hübl-Waller method agree with the calculated values. Cholesterol, however, yields an iodine value of 73 to 77 by the Hübl method and phytosterol a value of 50 to 68, according to the time of contact (five to forty-eight hours); when estimated by the Wijs method, the iodine value of these two substances is identical, namely, 135. A similar difference in values obtained by the two methods has also been noticed in the case of certain mineral oils. W. P. S.

**A New Method for the Detection of Methyl Alcohol.** REINO HÄMÄLÄINEN (*Acta Soc. Med. fennic. "Duodecim.,"* 1921, **3**, 1—6; *Ber. Ges. Physiol.*, **11**, 262—263; from *Chem. Zentr.*, 1922, ii, 918).—Formaldehyde from the oxidation of methyl alcohol by potassium permanganate in ethyl alcohol–sulphuric acid solution is detected by addition of methyl violet–sulphurous acid decolorised by oxalic acid; a dark- to light-blue coloration is formed. G. W. R.

**Estimation of the Alcohol Content of a Solution.** A. LÉVÊQUE (*Bull. Sci. Pharmacol.*, 1921, **28**, 549—554; from *Chem. Zentr.*, 1922, ii, 819).—The method of Rosset (A., 1921, ii, 598) is applied, using for miscibility temperature determinations, menthol, aniline sulphate, and phenol. G. W. R.

**Estimation of Glycerol by the Dichromate Method.** J. KELLNER (*Z. deut. Oel-Fett Ind.*, 1922, **42**, 345; cf. this vol., ii, 399).—Complete oxidation of glycerol by dichromate is effected only when sulphuric acid, *d* 1·230, is employed. Sodium chloride, if present in the glycerol, should be removed by treatment with lead acetate and silver oxide, since chlorine is evolved even with sulphuric acid, *d* 1·1. CHEMICAL ABSTRACTS.

**Chemical Reaction of Phenol.** ANGELO BELLUSSI (*Arch. Farm. sperim. Sci. aff.*, 1922, **33**, 190—191).—When 2 c.c. of 2% phenol solution is gently heated on a water-bath with a small crystal of ammonium phosphate or arsenate and a few drops of 3% hydrogen peroxide solution, a pink or cherry-red coloration appears after a few seconds, the phenol evidently undergoing oxidation. The same coloration is obtained, only far more tardily, when the phenol solution is heated with hydrogen peroxide or

even alone, so that the action of the ammonium phosphate or arsenate is catalytic in nature. T. H. P.

**Causse-Bonnan's Method for the Estimation of Dextrose.** H. J. LEMKES and L. M. LANSBERG (*Pharm. Weekblad*, 1922, **59**, 936—939).—It is confirmed that the results obtained vary considerably with the time occupied in titration. Attempts to get uniform results by substituting sodium for potassium compounds were unsuccessful. The white precipitate obtained at the end of the titration was found to contain Cu 23·05, Fe 11·2, K 21·55, (CN) 32·0, and water of crystallisation about 12·5%, but no empirical formula could be deduced. S. I. L.

**Modification of Bang's Method for the Estimation of Sugar in the Blood.** Z. ERNST and ST. WEISS (*Wiener klin. Wochschr.*, 1921, **34**, 174—175).—The blood sample of 0·115 c.c. is aspirated by means of a calibrated capillary pipette which is attached to a 15 c.c. flask, and the pipette is rinsed into the flask by aspirating through it Bang's diluting salt solution. The stopper and pipette are removed, the flask is filled with the salt solution to the mark, the contents are mixed, filtered and 13 c.c. of the filtrate, corresponding with 0·1 c.c. of blood, are analysed by Bang's method (A., 1918, ii, 278). Instead of the filtration, a centrifuge may be employed. CHEMICAL ABSTRACTS.

**The Estimation of the Total Oxygen-combining Power of the Blood in the Van Slyke Apparatus.** CHRISTEN LUNDSGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1922, **52**, 377—378).—The blood is saturated with oxygen after, instead of before, introduction into the apparatus. The remainder of the estimation is then carried out by the modified method of Van Slyke and Stadie (this vol., ii, 78). E. S.

**Qualitative and Quantitative Demonstration of Blood in Urine.** A. JOHANNESSEN (*Ugeak. Læger*, 1921, **83**, 1613; from *Physiol. Abstr.*, 1922, **7**, 280).—The reagent recommended is prepared by adding 1 gram of phenolphthalein and 25 grams of potassium hydroxide to 100 c.c. of distilled water and then boiling with 10 grams of zinc dust until decolorised. After filtration, an equal volume of 96% alcohol is added. This solution keeps for six months. Immediately before use 1 c.c. of hydrogen peroxide is added to each 9 c.c. Equal volumes of the reagent and the suspected urine are mixed; if blood is present up to 1 in 20,000 or 1 in 30,000 a pinkish-red colour is formed. With blood in water, a positive reaction is obtained with dilutions as high as 1 in 500,000. Copper, even in traces, interferes with the test. E. S.

# General and Physical Chemistry.

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**Influence of Pressure on the Refractive Index of some Organic Liquids.** F. Himstedt and Irma Wertheimer (*Ann. Physik*, 1922, [iv], **67**, 395—406).—The experimental arrangement of Röntgen and Zehnder was used, together with the Loewe-Zeiss interferometer. The refractive index and *dn*/*dp* were found for the following liquids, bromobenzene, chlorobenzene, nitrobenzene, chloroform, dichloroethylene, pinene, and hexane, and from these the compressibilities were calculated from the Newton, Beer, and Lorentz formulæ. The discussion of these values is postponed until the compressibilities of these liquids have been determined experimentally. W. E. G.

**The Establishment of the International System of Normal Wave-lengths.** Friedrich Müller (*Z. wiss. Photochem.*, 1922, **22**, 1—20).—Wave-lengths of the carbon, iron, and nickel spectra were accurately measured and are tabulated. Methods of measurement and precautions taken are given. W. T.

**Fine Structure of the Red Hydrogen Line.** Otto Oldenburg (*Ann. Physik*, 1922, [iv], **67**, 253—277).—Previous measurements of the Zeeman effect for $H_\alpha$ disagree among themselves and with the Sommerfeld quantum theory of fine structure. The divergences are shown to be mainly caused by errors arising in the photography of the spectrum from an echelon grating, and in the measurement of narrow diffuse bands. The true separation of $H_\alpha$ in the absence of a magnetic field, and at the temperature of liquid air, was obtained by resolution of the intensity curve into two Gauss curves. The value obtained was 0·140 Å.±0·008, whereas the measured distance between the two maxima was about 5% smaller. In weak fields (3500 gauss) the anomalous partial fusion of the *p*-components observed by Erochin was confirmed, but was shown to be due to a widening of the lines, without any appreciable alteration in the distance between the two components. At 18000 gauss, the two lines run together to form a single line which is narrower than the original doublet.

For weak fields, the Zeeman effect for the *s*-component is normal, but the widening of the lines at higher fields leads to the disappearance of the fine structure. Since the lines of H, $He^+$, and Zn, which are most sensitive to the Stark effect, also become diffuse in a magnetic field, it is possible that an unexpected Stark effect was present. However, this is unlikely, since no appreciable change in potential along the capillary tube was observed under the influence of the magnetic field. Also the widening of the lines caused by the Stark effect disappears on the application of a magnetic field. The Zeeman effect for small magnetic fields is normal,

but the fusion of the fine structure components observed in the higher fields is in opposition to the Sommerfeld theory.

W. E. G.

**The Balmer Series of Hydrogen.** E. GEHRCKE and E. LAU (*Ann. Physik*, 1922, [iv], **67**, 388—394).—Measurements of the fine structure of the Balmer series have been made at the temperature of liquid air, by means of a Lummer-Gehrcke interference spectroscope. The differences between the frequencies of the $H_\alpha$, $H_\beta$, and $H_\gamma$ doublets were, respectively, $\Delta\nu . 10^{-9}=8{\cdot}69$, 8·78, 8·74. These values were independent of the time of exposure, so that no error due to the contraction of the gelatin of the photographic plate could have occurred. A considerable deviation occurs between these values and the theoretical fine structure constant, 10·95, of Sommerfeld. It is shown that this deviation from theory is not explained by the additional hypothesis of Sommerfeld, which states that each line of the doublet is composed of a number of sub-components. The experimental results are also in poor agreement with the theory of Silberstein. It is remarkable that the mean figure for $\Delta\nu$ is that derived by Lenz from the Abraham assumption of stationary electrons. W. E. G.

**Series and Other Regularities in the Spectrum of Manganese.** MIGUEL A. CATALÁN (*Phil. Trans.*, 1922, 223A, 127—173).—The flame-arc, arc, and spark spectra of manganese have been photographed, using a Littrow spectrograph giving a linear dispersion of 16 Å. per mm. at λ 6300 and 5·5 Å. at λ 4700, a similar instrument with quartz prism giving a linear dispersion of 12 Å. per mm. at λ 4000, 4·5 Å. at λ 3000, and 2 Å. at λ 2300, and a concave grating ruled with 14438 lines per inch giving a normal dispersion of 5·5 Å. per mm. in the first order. It is shown that the flame, arc, and spark spectra of manganese, like those of other elements, are formed of two classes of lines, some belonging to the neutral atom and some to the ionised atom ($Mn^+$). In the spectrum of the neutral atom, triplet series and combination lines have been found. The series follows a Hicks formula with the Rydberg constant "$N$" and may be classified as follows: (*a*) A system of four triplets (sharp, diffuse, principal, and fundamental, the last two being rather doubtful), analogous to the ordinary triplet systems of series in the alkaline earths. (*b*) A system of three narrower triplet series (sharp, diffuse, and principal) which have strong analogies with the single line systems of series in the alkaline earths. (*c*) Another system of still narrower triplets (sharp, diffuse, and principal) which is parallel to the preceding system, the shift number being $C=10967{\cdot}75$. The intercombination lines, $1S-1p_2$ and $1S-1p_3$ (λ 5394·677 and λ 5432·555), between the first two systems are found as two lines very prominent at low temperatures, and losing very much of their intensity at high temperatures. The ionisation and resonance potentials of manganese have been calculated from the term 1S and from the wave number of the line $1S+1p_2$. The values obtained are 7·4 volts and 2·3 volts, respectively. The lines of ionised manganese, enhanced lines, also

form triplets. The data do not permit of the series being traced, but there is evidence that they include a system of triplets (sharp, diffuse, and principal), and also another system of narrower triplets, corresponding with the single line systems in the alkaline earths, as in the case of the neutral atom. Each diffuse triplet, in neutral and ionised atom alike, is formed of nine lines, giving five *d* terms in contrast to the six lines giving three *d* terms which are found in the more familiar diffuse triplets of the alkaline earths. In the spectra of both the neutral and the ionised atom there are certain groups of prominent lines having the same character and showing similar variations with changes of temperature. The lines of each group are related by very exact numerical separations, and these lines are denoted by the term *multiplet*. It is pointed out that similar multiplets exist in the spectra of the neutral atoms of magnesium, calcium, barium, strontium, ionised aluminium, scandium, yttrium, and lanthanum, and neutral atoms of silicon and chromium, and that they may represent a form of regularity present in the spectra of many elements, and serve to indicate the most probable nature of the series in the spectra where the actual series have not been traced. The spectrum of manganese is discussed in connexion with the position of manganese in the periodic system. It seems most probable that the neutral atom of manganese has two electrons in the outermost ring, and that when this atom loses an electron, thus becoming ionised, another electron from the next ring comes out to take its place in the outermost ring, which again contains two electrons. This mechanism would account for the similarity of the neutral and ionised manganese atoms. J. F. S.

**Ultra-red Characteristic Frequencies of the Silicates.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. tech. Physik*, 1922, **3**, 201—204; cf. this vol., ii, 179).—Since crystals containing $CO_3$ and similar groups show selective reflection which is characteristic of the group, and varies in a simple manner with the type of crystal, an analogous phenomenon was sought in the case of the silicates. The reflecting power of thirteen silicates was observed throughout the range 1 to 20 $\mu$, and twelve of these showed maxima near 10 $\mu$ and 18 $\mu$. These maxima were complicated, varying greatly from one substance to another, and could not be correlated with the crystal structure in the simple manner noted in connexion with other groups such as $CO_3$, $ClO_3$, etc. One specimen, analcite, lacked the maximum of greater wave-length. Two specimens containing the group $SiO_4$ showed no particular similarity in their reflexion curves. CHEMICAL ABSTRACTS.

**The Regularities of Ultra-red Spectra and the Failure of the Classical Dispersion Theory.** CLEMENS SCHAEFER (*Ann. Physik*, 1922, [iv], **67**, 407—419).—A theoretical paper. In the absorption spectra of polyatomic gases, a simple relationship occurs between the various bands. In diatomic gases, the band with short wave-length is almost exactly the octave of the band with long wave-length. Similar octaves are present in the

absorption bands of solid substances. An explanation is put forward based on the assumption that the molecular vibrations are asymmetrical, which supports the quantum theory and is opposed to the classical theory of dispersion and absorption. W. E. G.

**Absorption of Light by Sulphur at Various Temperatures.** MITSUHARU FUKUDA (*Mem. Coll. Sci. Kyōtō*, 1921, **4**, 351—354).—The absorption spectrum of a layer of sulphur 0·3 mm. thick, prepared by heating the element slowly until melted, extends from the ultra-violet up to $\lambda$ 0·408 $\mu$ at 0°, and extends a further 2 $\mu\mu$ towards the red end for every 10° rise of temperature up to 300°. No discontinuity, such as might be anticipated from the view of Kellas as to the constitution of the sulphur molecule (T., 1915, **113**, 903), was observed in the absorption spectrum at about 160°. The absorption spectrum of plastic sulphur depends on the initial temperature to which the sulphur is heated during its preparation. The higher this temperature, the further does the absorption extend from the ultra-violet towards the red end. J. S. G. T.

**Absorption of $\lambda$ 5460·97 Å. by Luminous Mercury Vapour.** J. C. MCLENNAN, D. S. AINSLIE, and (MISS) F. M. CALE (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 33—45).—It has been shown that when the radiation constituting the green line of mercury is passed through moderately luminous mercury vapour the main component and the components No. +1, $\Delta\lambda$=0·0086 Å. and No. −1, $\Delta\lambda$=−0·0087 Å. can be strongly absorbed. No marked absorption by luminous mercury vapour was observed in the case of the other nine components of the green line. Of the nine members constituting the magnetically resolved green line, it was found that the central undisplaced member was the only one that could be markedly absorbed by luminous vapour. It is also shown that absorption by luminous mercury vapour of the light constituting the green line in the mercury spectrum affords a means of clearly and easily demonstrating the existence of the components of the line with separations $\Delta\lambda$=+0·0182 Å. and $\Delta\lambda$=−0·021 Å., that is satellites Nos. +2 and −2. Some considerations are presented in support of the view that the components of the green line of mercury, for which $\Delta\lambda$=+0·0182 Å., +0·0086 Å., −0·0087 Å., −0·021 Å., and zero, may originate in atoms of the element having, respectively, the atomic weights 197, 198, 202, 204, and 200. J. F. S.

**The Absorption of Mercury Vapour.** J. FRANK and W. GROTRIAN (*Z. tech. Physik*, 1922, **3**, 194—197).—To test the theory that the absorption bands of mercury vapour are due to diatomic molecules, the absorption of the band at 2540 Å. was observed in superheated vapour. A sample saturated at 200°/20 mm. was observed at temperatures up to 1200°. The strength of the band was found to decrease with increasing temperature. A second sample, saturated at 240°/35 mm., showed greater absorption at low temperatures, but became nearly transparent at 1200°. This behaviour confirms the belief that the band is due to the molecule which is dissociated at high temperatures. From the rate of

variation of absorption with temperature, it is concluded that the work required for dissociation is of the order of one Cal. The number of molecules involved in the absorption is remarkably small, even at the lowest temperatures, where the partial pressure of molecules is less than $10^{-5}$ mm. CHEMICAL ABSTRACTS.

**A Simple Method for the Measurement of Ultra-violet Absorption.** CHR. WINTHER, BAGGESGAARD-RASMUSSEN, and E. SCHREINER (*Z. wiss. Photochem.*, 1922, **22**, 33—46).—The photographic method of Merton (T., 1913, **103**, 124) for the quantitative measurement of absorption has been adopted for the ultraviolet. An improved fluorometer has been constructed for extinction measurements of certain wave-lengths and the accuracy of the instrument has been tested by thermo-electric controls. The quantitative photographic method was employed for the investigation of the nitrates of potassium and silver, the results differed from those obtained by qualitative methods. W. T.

**The Emission of Light by Atoms.** K. FÖRSTERLING (*Z. Physik*, 1922, **10**, 387—392).—Previous experimental observations require that the light emitted by excited atoms is coupled with the atom in a continuous manner. This is contrary to the views of Sommerfeld, and in agreement with those of Mie. An external magnetic or electrical field does not appear to exert any effect on light free in the ether. Thus, if the emitted light is discontinuous, such fields should exert no effect on the radiated energy once it has left the electron. Those atoms in which the electrons have returned to an inner quantum orbit, after emitting the energy of excitation, should not show the Stark effect. The emitted light should be unchanged by the action of an electrical field and Stark, in his experiments, should have observed the unchanged line. For the *p*-components of $H_\alpha$, $H_\gamma$, and $H_\delta$ and for the *s*-component of $H_\delta$ this was shown not to be the case. On this account, the assumption is made that the electron in its passage from the initial to the final orbit should give up its light continuously to the ether. If the assumption of the spherical wave, and the correspondence principle of Bohr, are still maintained, it would appear necessary to postulate some new energy form in the atom. W. E. G.

**The Luminescence of Gas in the Electrodeless Discharge: The Induction Spectra of Cæsium and Rubidium.** M. L. DUNOYER (*J. Phys. Radium*, 1922, **3**, 261—292).—The vapours of cæsium and rubidium, when surrounded by a high frequency electromagnetic field, emit a brilliant luminescence at 100—300°. Rubidium vapour gives a feeble luminosity at the ordinary temperature, but no light can be detected from cæsium vapour below 90°. The colour of the luminescence of the saturated metallic vapour undergoes a sudden change at certain temperatures. It is uncertain to what extent this is due to an increase in density of the vapour. At the lowest temperatures, the induction spectra are very rich in lines, but the principal and secondary series are absent. At higher temperatures, all the cæsium and most of the

*rubidium lines which occur in the spark spectra appear, and a present in great intensity. The secondary series are, howeve completely absent, and only a few lines from the flame and ar* spectra are to be found in the induction spectra of these metals. The ionised atoms are believed to be the source of the induction spectra, and not the emission of an electron by the Bohr mechanism. Such ions should resemble the atoms of the rare gases, and points of resemblance should occur between the induction spectra of the two groups of elements. W. E. G.

**The Luminescence of Decomposing Ozone.** MAX TRAUTZ and WALTER SEIDEL (*Ann. Physik*, 1922, [iv], **67**, 527—572).—No chemiluminescence is observed when a carefully purified mixture of ozone and oxygen is heated to 400°. On the admission of coal gas to this mixture, light is emitted at the ordinary temperature, frequently with the formation of a mist. Purified air, carbon dioxide, and hydrogen do not give rise to this effect. Carbon monoxide when mixed with ozone produces chemiluminescence at temperatures above 150°, and a band of light is emitted between the wave-lengths 400 and 560 $\mu\mu$. This spectrum is independent of the thickness of the radiating gas.

The light emitted by mixtures of carbon monoxide and ozone is measured by means of an argon-filled rubidium cell. By a streaming method, it was shown that the amount of light is proportional to the product of the concentrations of the two gases; thus $\Delta a = K_1[CO][O_3]/1+K_2[O_3]/t$, where $\Delta a$ is the electrometer deflexion, $K_1$ and $K_2$ are constants depending on the velocities of two simultaneous reactions, and $t$ is the time of streaming for 50 c.c. of gas. These conclusions were confirmed by a study of the reaction in a stationary gas mixture. The velocity of emission of light obeys the second order law, and the deviations which were observed are probably due to irregularities in the temperature of the gas mixture. The velocity of emission increases with increase in temperature, but the total quantity of light emitted increases to a limiting value. The law of constant light summation propounded by Lenard for phosphorescent substances (*Heidelb. Akad.*, 1912, A, 5 Abh.) applies equally well to the chemiluminescence from the mixture of carbon monoxide and ozone, the quantity of light being independent of both the velocity and the temperature. The presence of indifferent gases such as nitrogen or carbon dioxide is without effect on the emission of light. The conclusion that the reaction is of the second order is supported by the observations of Angerer (A., 1921, ii, 257) on the decomposition of $N_3$. W. E. G.

**Catalysis. XVI. Radiation as a Factor in Thermal and Photochemical Reactions.** N. R. DHAR (*Z. anorg. Chem.*, 1922, **122**, 151—158).—The author has studied the velocity of certain chemical reactions in tropical sunshine and found that the light waxs accelerated the reaction in all cases, more particularly so in sampcase of those reactions with a high temperature coefficient. low teimer concludes with a brief review of the radiation hypothesis. behaviou. W. T.

**The Effect of Colloids on Silver Bromide Emulsions.** ROBERT SCHWARZ and HEINRICH STOCK (*Z. wiss. Photochem.*, 1922, **22**, 26—32).—The influence of catalysts on the photochemical decomposition of pure silver bromide has been investigated, the amount of decomposition being determined by the method previously described (A., 1921, ii, 614). Platinum sol delays the inversion point and solarisation. Silver and silicic acid sols act as positive catalysts, whilst aluminium hydroxide has a negative effect. Ferric hydroxide and stannic acid coagulated the emulsion. W. T.

**The Photochemical Reduction of Titanium Salts.** A. BENRATH and A. OBLADEN (*Z. wiss. Photochem.*, 1922, **22**, 65—71).—The sulphate and oxalate of titanium were not reduced by ethyl alcohol on long exposure to light, whereas the chloride reacted violently. For quantitative work, ethyl alcohol was an unsatisfactory reducing agent owing to the formation of hydrogen peroxide. Mandelic and lactic acids were found to be suitable, and measurements were carried out with the former, which was the more powerful reducing agent. The temperature coefficient of the reaction for 10° was found to be 2·21. The reaction obeyed the law of mass action, and was found to be bimolecular. Chlorides decreased the velocity, probably owing to the decrease of ionisation of the tetrachloride. W. T.

**Elimination of Carbon Dioxide from Organic Compounds. VI. The Action of the Light of the Electric Arc on Aqueous Oxalic Acid Solutions in Presence of Ferric, Chromic, and Mercuric Chloride, of Uranyl Acetate, and of Iodic Acid.** HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. Deut. pharm. Ges.*, 1922, **32**, 209—216; cf. this vol., i, 6).—Many observations are recorded on the action of sunlight in decomposing aqueous solutions of oxalic acid, but none on the effect of artificial light. Experiments have been made on the decomposing effect of the light from an electric arc on oxalic acid in presence of a number of "catalysts." In presence of ferric chloride, 61·7% of the oxalic acid was decomposed into carbon dioxide in sixteen hours, the reaction being represented by the equation $H_2C_2O_4+Fe_2Cl_6=2FeCl_2+2HCl+2CO_2$. When chromic chloride was used, no decomposition occurred, but ammonium oxalate was oxidised in presence of mercuric chloride, the latter being reduced to mercurous chloride. The decomposition of oxalic acid was also promoted by uranyl acetate and by iodic acid, in the latter case with formation of free iodine. So far as qualitative experiments show, sunlight and the arc light are equivalent for the decomposition of oxalic acid in presence of the above substances. E. H. R.

**Chemistry of Actinometers.** A. BENRATH, E. HESS, and A. OBLADEN (*Z. wiss. Photochem.*, 1922, **22**, 47—64).—The mercuric chloride–ammonium oxalate actinometer was found to be trustworthy within narrow limits only. The ferric chloride and the oxalic acid–uranyl acetate actinometers were found to be in good agreement. Electrolytes retard the reduction of ferric chloride

and the decomposition of oxalic acid. The authors argue that tl added electrolytes have no influence on the photochemical reactio but decrease the dissociation of the iron salt and the oxalic aci and they draw the conclusion that the ferric ion and the oxala ion are photochemically active, whilst the undissociated molecul are inactive. W. T.

**The Photoelectric Effect of the Alkaline-earth Phosphor** Karl Göggel (*Ann. Physik*, 1922, **67**, 301—319).—The relatic between the photoelectric effect and the wave-length of the excitir light have been studied for CaBiα and SrBiα phosphors (cf. Lena and Saeland, A., 1909, ii, 283). In order to maintain the phosph in a condition of least excitation, it was illuminated simultaneous by the exciting radiation, and by either green or red light. C account of the low conductivity of the phosphor as compared wi the metals, the photoelectric effect of these substances increas more slowly than the intensity of the exciting light. The norm photoelectric effect becomes appreciable at the violet end of th visible spectrum, and increases rapidly with decrease in wav length. In addition, in the region of the wave-length of the phos phorescent light, selective effects are observed, which are especiall large in the presence of green light. In the case of the CaBi phosphor, the maxima for the photoelectric effect correspon exactly with the maxima of phosphorescence, but a shift of th photoelectric effect towards the red occurs with the SrBiα phospho The normal phosphors show a much greater photoelectric effect an phosphorescence than the decinormal phosphors. This is asso ciated with the larger number of small phosphorescence centres i the normal phosphor. Phosphors when destroyed by pressur in the presence of light, become coloured, show practically n phosphorescence, and give the normal photoelectric effect. Whe destroyed in the dark, however, a much larger effect is obtaine which decreases with time. It is suggested that this is caused b the destruction of the closed chain compounds forming the phos phorescence centres, into molecules containing free valency elec trons. The magnitude of the photoelectric effect is proportiona to the amount of the colouring of the phosphor.

The *d*- and *u*-emission of phosphorescent light is accompanie by the separation of electrons, whereas the *m*-emission, the fluores cence, is not accompanied by a photoelectric effect, and hence i not a consequence of electron emission. The electrons emitte from a phosphorescence centre do not necessarily return to the sam centre or by the same path. W. E. G.

**β-Ray Spectra and their Connexion with γ-Radiation** Lise Meitner (*Z. Physik*, 1922, **11**, 35—54).—By means of a mor precise investigation, it is shown that the thorium-*B* line, whic was previously and erroneously classified as a line belonging to th $L_2$ ring (this vol., ii, 416), in reality belongs to a second γ-radiation group, as was indicated by Ellis (A., 1921, ii, 422). Measurements of thorium-*C* and thorium-*C''* confirm those of von Baeyer, Hahn, and Meitner (A., 1911, ii, 567) as to the existence of a group of

β-rays of velocity about 95% that of light, which Ellis (*loc. cit.*) was unable to find, and, further, these measurements show that on using the exact energy of the *K*-disintegration of thallium some of these lines must be interpreted otherwise than was done by Ellis. Very exact experiments with radium-*D* which have been controlled by photometric registration show that the three *L* levels found by Ellis are not present in radium-*D*; one only could be found and that is the $L_2$ level. It is concluded from the above-mentioned results and those of Ellis for radium-*B* that in the excitation of the characteristic radiation by γ-radiation proceeding from the nucleus of the atom itself practically only the $L_2$ level is affected, in contrast to the relationships in the excitation by Röntgen rays from outside the atom. An attempt is made to explain this result on the basis of the unsymmetrical atomic configuration postulated in Bohr's hypothesis. The criticism of the author's interpretation of the β-change put forward by Ellis is discussed, and it is shown that this interpretation is in keeping with the experimental facts.

J. F. S.

**Wave-lengths of γ-Rays.** Lise Meitner (*Naturwiss.*, 1922, **10**, 884; from *Chem. Zentr.*, 1922, i, 1352—1354; cf. this vol., ii, 416).—The lattice of crystals is too coarse for the determination of the wave-length of hard γ-rays. Primary β-rays from the disintegration of an atomic nucleus have in the simplest case uniform velocity, and energy corresponding with this velocity. The β-radiation may either pass out of the atom with unchanged velocity or else γ-rays may originate in the nucleus from the β-rays, having the same energy and the relation $E_\beta = h\nu_\gamma = hc/\lambda_\gamma$ (1) holds. The resultant γ-radiation detaches *K*-, *L*-, and *M*-electrons from the atom in which it originates and the energy of this secondary radiation is equal to the energy of the γ-radiation, less the energy used for disintegration or $h\nu_\gamma = E^k{}_\beta - E_k$ (2), where $E_k$ is the energy used in detaching *K* electrons. $E_\beta$ and $E^k{}_\beta$ may be determined from the deviation of the β-rays in a magnetic field, and $E_k$ from the *K*, *L*, and *M* absorption wave-lengths obtained by the lattice method. Applying equations (1) and (2), the author found the wave-length of the γ-rays from thorium-*B* to be $5{\cdot}2 \times 10^{-10}$ cm., those from radium $6{\cdot}6 \times 10^{-10}$ cm., and those from radium-*D* $2{\cdot}9 \times 10^{-9}$ cm. The shortest wave-length obtained by this method was that of the γ-rays from thorium-*C''*, namely, $2{\cdot}45 \times 10^{-10}$ cm., approximately one-fifth of the wave-length of the shortest characteristic Röntgen rays. γ-Rays of even shorter wave-length may be expected to occur. The γ-rays originating from the nucleus may in some circumstances have a greater wave-length than the corresponding *K*-series. In the case of radium-*D* where the wave-length of the *K* series is $1{\cdot}385 \times 10^{-9}$, the γ-rays cannot set free any *K* electrons.

G. W. R.

**Excitation and Ionisation Potentials of Neon and Argon.** G. Hertz (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 179—187).—The excitation potentials of argon and neon have been

determined by plotting the number of electrons which have a velocity below a definite small value (in the present experiments that below the velocity corresponding with 0·2 volt) against the applied tension. In this way, the excitation potentials are shown as sharp maxima in the curves. This method is unsuitable for measuring the ionisation potential, and a new method for measuring this quantity has been employed. The results show that, starting from the value 20·45 volts as the lowest excitation potential of helium, two pronounced excitation potentials are found at 17·35 and 19·15 volts for neon. The ionisation potential of neon is found to lie at 22·2 volts. In the case of argon, excitation potentials are found at 12·25 and 13·7 volts and the ionisation potential at 16·0 volts. It is shown in the case of neon that the values found are in harmony with the optical measurement of the spectrum, and, further, there is no room in the series spectrum for a resonance potential of 11·8 volts and ionisation potentials at 16·7 and 20 volts, as found by Horton and Davies (A., 1919, ii, 210), neither did the author find any indication of a resonance potential or ionisation potentials at the values stated. In the case of argon, a comparison with the series spectrum is not possible, but assuming that the argon spectrum is constituted similarly to the neon spectrum, then calculating from the observed excitation and ionisation potentials, the following mean values for the first groups of the terms are to be expected: $0{\cdot}5s=130000\pm1000$, $1{\cdot}5s\sim30400$; $2p\sim18600$, and higher terms $<10500$. J. F. S.

**Chemical Reactions induced by the Corona Effect in Circuits traversed by Continuous Currents.** C. Montemartini (*Gazzetta*, 1922, **52**, ii, 96—97).—The corona discharge is capable of effecting the following reactions: Formation of ozone from air; decomposition of carbon dioxide into carbon monoxide and oxygen; synthesis of ammonia from its elements; formation of carbon dioxide and hydrogen from carbon monoxide and water vapour; formation of hydrogen cyanide from acetylene and nitrogen; formation of formaldehyde from carbon dioxide and hydrogen; formation of benzoic acid from carbon dioxide and benzene vapour; decomposition of hydrogen sulphide into its elements and the inverse reaction; decomposition of hydrogen antimonide and its synthesis from its elements. T. H. P.

**Resistance Temperature Coefficient of Concentrated Solutions of Sodium in Liquid Ammonia.** Charles A. Kraus and Walter W. Lucasse (*J. Amer. Chem. Soc.*, 1922, **44**, 1941—1949).—The resistance temperature coefficients of concentrated solutions of sodium in liquid ammonia have been measured from the saturation point up to $V=5{\cdot}02$ and at temperatures from the boiling point of liquid ammonia down to $-60°$. Near the saturation point, the temperature coefficient of sodium in liquid ammonia has a value approximately 0·066%. With decreasing concentration, the temperature coefficient increases markedly, passing through a maximum value of approximately 3·6% at $V=1{\cdot}1$ and then decreasing to a value of approximately 1·55 at dilutions above 4·0 litres

per atom. Taking into account the earlier work on the temperature coefficient of more dilute solutions, it is evident that the temperature coefficient passes through a minimum value. From the form of the curve at high concentrations, the temperature coefficient is seen to be approaching a negative value at high concentrations, although this value is not actually realisable, since the saturation point of the solution is reached. At the highest concentrations the solutions of the metals in liquid ammonia closely resemble metallic alloys. At lower temperatures, the temperature coefficient increases markedly at higher concentrations. As the concentration decreases, the influence of temperature on the coefficient decreases, and at a dilution $V=5{\cdot}3$ the coefficient is relatively independent of temperature. From previous work on the influence of temperature on the temperature coefficient of more dilute solutions, it is clear that the influence changes sign, since at low concentrations the coefficient increases markedly with increasing temperature. J. F. S.

**Effect of Substitution on the Free Energy of Oxidation-reduction Reactions. I. Benzoquinone Derivatives.** VICTOR K. LAMER and LILLIAN E. BAKER (*J. Amer. Chem. Soc.*, 1922, **44**, 1954—1964).—The oxidation reduction potentials of the substituted derivatives of quinone–quinol mixtures have been determined at 25°. The method consisted in adding the quinone to a measured volume of buffer solution, removing the oxygen by nitrogen, and then reducing a portion of the quinone to quinol with titanium chloride solution and measuring the potential of the mixture against a calomel electrode, using gold or platinum electrodes. Other measurements were made starting with the quinol and oxidising it with potassium dichromate. The concentration of hydrogen ions was also measured in each solution. The cells measured were therefore of the types: $Hg\,|\,Hg_2Cl_2,KCl(sat)\,||\,Q+QH_2(yM)+H^{\cdot}(xM)/Pt$; and $Hg\,|\,Hg_2Cl_2,KCl(sat)\,||\,H^{\cdot}(xM)\,|\,H_2(1\ atm.)Pt$. The following values of the normal potentials and the reduction of free energy in the various cases are recorded: bromo-*p*-benzoquinone, 0·7151 volts, 138·0 kilojoules; chloro-*p*-benzoquinone, 0·7125, 137·5; *p*-benzoquinone, 0·6990, 134·9; toluquinone, 0·6454, 124·6; *p*-xyloquinone, 0·5900, 113·9; *p*-thymoquinone, 0·5875, 113·4; dimethoxy-*p*-benzoquinone, 0·5139, 99·2; naphthaquinone, 0·4698, 90·7. The effect produced by the substitution of the various groups is discussed in the light of the positive–negative rule of Michael. The validity of the method of work adopted has been established by (1) the constancy and reproducibility of the potentials under widely varying concentrations and following anodic or cathodic polarisation, (2) the use of different electrodes, (3) the agreement of the *E.M.F.* with those obtained by the method of pure mixtures, and (4) the approach of the equilibrium from both sides. The *E.M.F.* values are reproducible to 0·2 milli-volt. J. F. S.

**Stability of Phthalate Solutions as Standards in Hydrogen-ion Work.** C. J. WOOD and P. P. MURDICK (*J. Amer. Chem. Soc.*, 1922, **44**, 2008—2009).—An answer to the criticisms of Oakes

and Salisbury (this vol., ii, 468), who have shown that phthala solutions when measured against a hydrogen electrode a drift the *E.M.F.* is observed (cf. also Merrill, this vol., i, 326). Th authors have repeated their measurements with a 0·2*M*-solutic of potassium hydrogen phthalate, which are shown to agree wit those of Clark ("Determination of Hydrogen Ions," Baltimor 1920). It is therefore contended that potassium hydrogen phthalat may be obtained in a sufficiently pure state to give constant poter tials with the hydrogen electrode. J. F. S.

**An Electrolytic Current Intensification Effect, A Ne Electrolytic Displacement Effect, and the Connexion betwee Electrolysis and the Emission of Electrons in a Vacuun III.** D. REICHINSTEIN and M. ROTHSCHILD (*Z. physikal. Chem* 1922, **102**, 209—234; cf. A., 1921, ii, 729, this vol., ii. 112).— continuation of previous work. It is shown that the new displac ment effect makes clear the mechanism of electrolytic detecto with a subsidiary source of current. It is shown experimentall that in such detectors the mechanism does not depend on a co version into direct current, but that these detectors act as curre intensifiers; the ratio of the direct current energy brought int existence by an alternating current to that of the alternating curre itself may be greater than eighty-eight. An account is given a new condenser commutator effect. A new electrolytic detect is described which does not make use of an external subsidiar current; this is characterised by the fact that in the absence an alternating current it has an *E.M.F.*=0. An electrical curre is capable of bringing about a reaction in an electrolyte withou making any use of the migrations of the ions. When the ne intensifier is connected with a source of alternating current, i intensifies the entering current one thousand times, consequentl the intensifier and detector can be directly connected with th antennæ which collect high frequency undamped oscillations.

J. F. S.

**The More Recent Conception of Electrolytes. IV. Th *Dissociation State of Acids of Medium Strength*, especiall Dichloroacetic Acid in Water and in Salt Solutions.** ERLIN SCHREINER (*Z. anorg. Chem.*, 1922, **122**, 201—235).—Pure dichlor acetic acid was prepared and was found to be dimorphous wit m. p. 12·15° and 13·25°, $d_{15}^{15}$=1·5727. The *E.M.F.* of this ac was measured in aqueous solutions as well as in 0·2 molar solution of potassium chloride, sodium acetate, and magnesium sulphat The quinhydrone electrode was used (Biilmann, A., 1921, ii, 372 The conductivities of the acid and its sodium salts were als measured. Assuming the activity constant of the hydrogen io to be 0·2, that of the dichloroacetate ion was found to be 0·3 Calculations based on the *E.M.F.* measurements and on the con ductivity measurements were in complete agreement with th general law of mass action. W. T.

**Chromate Electrolysis with Diaphragms.** A. LOTTERMOSE and KURT FALK (*Z. Elektrochem.*, 1922, **28**, 366—376).—Whe

sodium chromate is electrolysed in a two or three compartment cell, the current yields of sodium dichromate and sodium hydroxide theoretically possible depend on the composition of the solutions originally present in the anode and cathode compartments. It was shown by Müller and Sauer (A., 1912, ii, 1037) that if the anolyte is a solution of sodium chromate and the catholyte one of sodium hydroxide, the yields are lower than they are when sodium chromate is used in both compartments. Their conclusions are now confirmed by extended observations on two compartment cells of the above types and on three compartment cells (*a*) with sodium hydroxide as the catholyte and sodium chromate in the other two compartments, and (*b*) with chromate in all three. The best yields of dichromate are obtained under the last conditions, as circumstances are then the least favourable for the migration of hydroxyl-ions into the anode compartment. The paper concludes with a mathematical discussion of the possible yield obtainable with these types of cell both with and without taking account of the influence of diffusion. [See *J. Soc. Chem. Ind.*, 1922, 857A.]

E. H. R.

**Thermal Expansion of Concentrated Salt Solutions.** ROBERT MEYER (*Physikal. Ber.*, **3**, 149; from *Chem. Zentr.*, 1922, i, 1214—1215).—The thermal expansions of aqueous solutions of sodium nitrate, potassium nitrate, zinc sulphate, and potassium carbonate, saturated at 20—70°, were measured at temperatures up to 90°. The coefficient of expansion of concentrated solutions increases with rise of temperature, but whilst in the case of water the rate of increase of the coefficient of expansion decreases smoothly with rise of temperature, the curves obtained for concentrated salt solutions are irregular and show points of inflexion the positions of which depend on the concentration of the solution. G. W. R.

**Approximate Rule for the Specific Heats of Gases and Vapours.** RUDOLF MEWES (*Z. Sauerstoff Stickstoff Ind.*, 1922, **14**, 26; from *Chem. Zentr.*, 1922, i, 1129—1130).—From the formulæ $cp_t = cp_0(1+\gamma)^t$ and $cp_t/cp_0 = (c'p_t/c'p_0)^n$ the specific heat of a substance can be calculated for all temperatures. Values are given of log $(1+\gamma)$ and $n$, respectively, for a number of gases and vapours. The values of log $(1+\gamma)$ are simple multiples of each other, whilst the values of $n$ are simple integers. G. W. R.

**The Specific Heats of Gases with Special Reference to Hydrogen.** CHRISTOPHER KELK INGOLD and EDITH HILDA USHERWOOD (T., 1922, **121**, 2286—2291).

**The Isotherms of Nitrogen, Oxygen, and Helium.** L. HOLBORN and J. OTTO (*Z. Physik*, 1922, **10**, 367—376).—The isothermals of oxygen and nitrogen at temperatures of 0°, 50°, and 100°, and at pressures up to 100 atm., and of helium from 50 to 100 atm. have been determined (cf. A., 1915, ii, 743; 1921, ii, 15). The coefficients are given for the equations $pv = A + Bp +$

$Cp^2$, and $pv=(pv)_0(1+B'/v+C'v^2)$; the $pv$ values for helium may be expressed by a linear relationship.

| | | $A$. | $B$ 10³. | $C$ 10⁶. | $B'$ 10³. | $C'$ 10⁶. |
|---|---|---|---|---|---|---|
| Nitrogen... | 0° | 1·00057 | −0·58100 | 4·76327 | −0·57070 | 4·58106 |
| | 50° | 1·18368 | −0·02500 | 3·80816 | −0·03281 | 4·79200 |
| | 100° | 1·36682 | +0·36057 | 3·15102 | +0·35016 | 4·98088 |
| Oxygen ... | 0° | 1·00130 | −1·30143 | 0·46452 | −1·27335 | 4·07229 |
| | 50° | 1·18456 | −0·63543 | 0·27755 | −0·62750 | 3·26394 |
| | 100° | 1·36782 | −0·20357 | 0·22571 | −0·20149 | 3·02964 |
| Helium ... | 0° | 0·99930 | +0·69543 | — | +0·69565 | 0·50594 |
| | 50° | 1·18223 | +0·68887 | — | 0·68797 | 0·51689 |
| | 100° | 1·36518 | +0·66804 | — | 0·67453 | 0·53306 |

Amagat's $pv$-values for 100 atm. are greater by 0·7% for nitrogen and 0·3% for oxygen, and the results of Kamerlingh Onnes and Hyndman for oxygen are, at the lower pressures, about 0·4% greater and, at the higher pressures, about the same amount smaller. The $pv$-values for air have been calculated for air from those for oxygen and nitrogen: the differences between these and the experimental values for air are within the error of the observations, except at 0° and 50° for the higher pressures. W. E. G.

**Thermodynamic Treatment of the Possible Formation of Helium from Hydrogen.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 1902—1908).—A theoretical paper in which it is shown that by combining the older ideas as to the possible formation of helium from hydrogen with the newer ideas as to the entropy of monatomic gases, it becomes possible to subject the reaction 4H=He to complete thermodynamical treatment. The equilibrium constant calculated from this treatment shows that hydrogen should combine practically completely to form helium at all temperatures below a million degrees and pressures above $10^{-100}$ atmospheres. The conflict between this conclusion and the mutual presence of hydrogen and helium under solar, stellar, and terrestrial conditions has been discussed. Of the various possibilities presented for reconciling the thermodynamic conclusion as to equilibrium constant and the facts, the author regards the following as most hopeful; (1) the reaction to form helium from hydrogen is an extremely slow one even at 20000°, (2) hydrogen consists of a mixture of isotopes one of which has an atomic weight nearly unity, and (3) helium is decomposed in the sun and stars by the action of an extremely short wave-length radiation which is so penetrating as not to be in temperature equilibrium with the helium affected. J. F. S.

**Correlation of Entropy and Probability.** GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1922, **44**, 1881—1886).—In a recent paper (this vol., ii, 257), the author has put forward two equations, the one $S=C\infty/K.\log C\infty/(C\infty-C)$, connecting entropy and probability, and the other, $C=C\infty kT^K/(kT^K+1)$, connecting specific heats and temperature. The validity of the former equation was substantiated for eighteen substances and the latter equation by a single example. In the present paper the second equation has been shown to hold for the specific heat of all substances which

have been measured by the thermo-electric methods. The results calculated for thirty-one substances agree with the experimental values in many cases better than the individual experiments agree with one another. Only in the case of ice and silver iodide is the agreement poor, and here it is shown that the specific heat data are quite erroneous. J. F. S.

**The Relation of Melting Point to Boiling Point.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1922, **122**, 51—60).—The ratio of the absolute melting point to the normal boiling point has been calculated for 412 elements and compounds (inorganic and organic).

| No. of cases. | Ratio. | No. of cases. | Ratio. | No. of cases. | Ratio. |
|---|---|---|---|---|---|
| 1 | 0·198 | 118 between | 0·5—0·599 | 25 between | 0·8—0·899 |
| 14 between | 0·3—0·399 | 99 „ | 0·6—0·699 | 26 „ | 0·9—0·999 |
| 66 „ | 0·4—0·499 | 61 „ | 0·7—0·799 | 2 above | 1·0 |

The mean of all the ratios (A) was found to be 0·62, or taking only those shown to occur more frequently (4, 5, 6, 7) the mean (B) was 0·5946. The following are the quotients for the different categories examined. Elements (A) 0·5583, (B) 0·4542. Inorganic compounds (A) 0·7183, (B) 0·6857. Organic compounds (A) 0·5839, (B) 0·5745. W. T.

**Fused Salts.** W. HERZ (*Z. Elektrochem.*, 1922, **28**, 390—391).—It has been shown that at the critical temperature the refractive index of non-associated liquids is a constant, 1·126 (A., 1921, ii, 529; this vol., ii, 97). From the measurements of Meyer and Heck of the molecular refractions of fused potassium and sodium nitrates (this vol., ii, 241), the critical refractive indices have been calculated and are, respectively, 1·136 and 1·138. It appears probable, therefore, that the requirements of the theory are fulfilled by fused salts. The critical densities, calculated from the law of corresponding states, are, respectively, 0·599 and 0·612. The boiling points of the alkali fluorides calculated by Lorenz and Herz from the surface tensions (this vol., ii, 261) are compared with the values found by von Wartenberg (this vol., ii, 146). The agreement is good except in the case of cæsium fluoride. The critical pressures of the alkali fluorides, chlorides, bromides, and iodides are now calculated from the known relation between surface tension at the boiling point and critical pressure, $\gamma_s=0{\cdot}427p_k$. The values obtained are probably minimum values. They are used to calculate the constant of Cederberg's vapour pressure formula. When the differences between melting and boiling points of the alkali haloids are compared, regular variations are found as the atomic weight of the metal or halogen increases. E. H. R.

**The Vapour Pressure of some Salts. III.** H. VON WARTENBERG and O. BOSSE (*Z. Elektrochem.*, 1922, **28**, 384—386).—Continuing the work previously described on the vapour pressures of salts (this vol., ii, 156), the following new data have been obtained. Silver chloride, m. p. 449°, b. p. 1554°, $\log p = -44257/4{\cdot}571T +$

5·298. Cuprous chloride, m. p. 430°, b. p. 1367°, $\log p = -19258/4{\cdot}571T + 2{\cdot}573$. Cuprous bromide, m. p. 483°, b. p. 1345°, $\log p = -19075/4{\cdot}571T + 2{\cdot}5794$. Cuprous iodide, m. p. 588°, b. p. 1293°, $\log p = -19257/4{\cdot}571T + 2{\cdot}690$. Lead chloride, m. p. 498°, b. p. 954°, $\log p = -28518/4{\cdot}571T + 5{\cdot}085$. Lead bromide, b. p. 916°; $\log p = -28180/4{\cdot}571T + 5{\cdot}183$. Lead fluoride, m. p. 818°, b. p. 1292°, $\log p = -39425/4{\cdot}571T + 5{\cdot}510$. Thallous chloride, m. p. 430°, b. p. 806°; $\log p = -25108/4{\cdot}571T + 5{\cdot}093$. Thallous bromide, m. p. 456°, b. p. 815°, $\log p = -25164/4{\cdot}571T + 5{\cdot}059$. Thallous iodide, m. p. 440°, b. p. 824°, $\log p = -25168/4{\cdot}571T + 5{\cdot}021$. Thallous fluoride, b. p. 298°, $\log p = -25152/4{\cdot}571T + 9{\cdot}639$. The thallous salts are abnormal in that the iodide has the highest boiling point and the fluoride the lowest. No vapour pressures of barium chloride, calcium chloride, calcium bromide, and boric anhydride could be measured at the highest attainable temperature, 1536—1546°. The opinion previously expressed that the fluorides form double vapour molecules is now withdrawn, an experimental error having been detected. The dissociaton temperatures of the following acid fluorides were determined: lithium hydrogen fluoride, below 200°; sodium hydrogen fluoride, about 270°; potassium hydrogen fluoride, 310—440°; cæsium hydrogen fluoride, 500—600°; rubidium hydrogen fluoride, 550—670°. E. H. R.

**Calorimetric Determinations.** P. E. VERKADE (*Chem. Weekblad*, 1922, **19**, 389—393; cf. this vol., ii, 474).—The Third Conference of the International Union of Pure and Applied Chemistry, held at Lyon, June—July, 1922, recommended for the standardisation of calorimetric bombs the use of pure benzoic acid, prepared by the Bureau of Standards at Washington, and tested calorimetrically before issue; this special material is obtainable from the Bureau of the Institut International d'Etalons physico-chimiques at Brussels (The University, Rue des Sols). The other materials generally employed are reviewed, and the values given for the heats of combustion criticised. Pending exact determination of the mechanical equivalent of heat, which will permit of electrical measurements for standardisation, the Brussels benzoic acid should be used for all thermo-chemical determinations. The heat of combustion accepted by the Conference is 6324 cal. per gram weighed in air at 15° (6319, weighed in a vacuum). S. I. L.

**Apparatus for the Rapid Determination of the Specific Gravity of Small Amounts of Liquid.** ERICH WIEDBRAUK (*Z. anorg. Chem.*, 1922, **122**, 167—170).—Water and the liquid in question are contained in two communicating U-tubes which also communicate with a manometer, the heights of the liquids which balance various pressures are measured, and hence the specific gravity is calculated. W. T.

**Kinetic Theory of Adsorption.** D. C. HENRY (*Phil. Mag.*, 1922, [vi], **44**, 689—705).—A theoretical paper in which a kinetic theory of adsorption of gases has been developed by means of assumptions derived from Langmuir's conception of a unimole-

cular layer. Equations for the adsorption isotherm and isostere are deduced which are in keeping with experimental results. A method is suggested for applying these equations to adsorption from solution, and the results are compared with experimental data. A theoretical derivation of the well-known exponential formula is given which attributes a theoretical significance to the index $1/n$, which is in qualitative agreement with experimental data. J. F. S.

**Adsorption of Activated Sugar Charcoal. I.** F. E. BARTELL and E. J. MILLER (*J. Amer. Chem. Soc.*, 1922, **44**, 1866—1880).—The adsorption of methylene-blue, a basic dye of the electrolyte type, by activated ash-free sugar charcoal has been investigated. The results show that this adsorption is partly, if not entirely, hydrolytic in character. Ash-free sugar charcoal will completely adsorb a certain maximum amount of methylene-blue from solution and still leave the solution neutral. During this process of adsorption a considerable quantity of hydrochloric acid is set free *which is readily and completely adsorbed. Adsorption of quantities* of methylene-blue greater than the above-mentioned maximum results in the liberation of hydrochloric acid which is not subsequently removed from solution by adsorption. The contradictory results obtained by previous investigators who have used blood charcoal as adsorbent have been reproduced with pure sugar charcoal and an explanation of these results is put forward.
J. F. S.

**Adsorption and Catalysis in Fuller's Earth.** ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS (T., 1922, **121**, 2119—2123).

**Adsorption and Orientation of the Molecules of Dibasic Acids and their Ethereal Salts in Liquid–Vapour Interfaces.** H. H. KING and R. W. WAMPLER (*J. Amer. Chem. Soc.*, 1922, **44**, 1894—1902).—Surface tension measurements have been made at 20° by the drop-weight method of aqueous solutions of a series of concentrations of tartaric, malonic, succinic, fumaric, oxalic, malic, and maleic acids and the diethyl esters of the four first-named acids. The adsorption has been found for each solution by means of the Gibbs equation $u=-1/iRT\,.\,\delta\gamma/\delta\log C$. A general explanation of the chemical theory of capillarity is given and this is shown to serve as an explanation of catalysis. Tables are drawn up giving the adsorption, surface tension, drop weight, and density of all the above-named solutions. It is shown that the adsorption of *the dibasic acids is less than that of the monobasic acids*; the degree of adsorption of the dibasic acids increases with increasing carbon content, but the increase is not regular for each carbon atom added to the chain. The presence of a hydroxyl group in the molecule decreases the amount adsorbed, and raises the surface tension, as shown by malic and *d*-tartaric acids. The esters are adsorbed more than the acids, due to the replacement of the polar carboxyl group by the group $-C(=O)\rightarrow O-C_2H_5$. The molecules are oriented

in the surface with the polar groups in the liquid and the least active portions of the molecule forming the surface. J. F. S.

**The Rate of Absorption of Carbon Dioxide by Ammoniacal Solutions.** PAUL RIOU (*Compt. rend.*, 1922, **175**, 472—474).—Investigation of the influence of temperature and of concentration on the rate of absorption of carbon dioxide by solutions of ammonium carbonate and hydrogen carbonate shows that at constant temperature it increases to a maximum with increase of concentration. In the presence of ammonium hydrogen carbonate, the absorption velocity is considerably less and a decrease takes place with higher concentration after the maximum has been reached. With increase of temperature, a maximum rate is also obtained; the presence of a larger proportion of hydrogen carbonate in the solution corresponds with a reduction in the temperature at which this maximum is reached. H. J. E.

**Cataphoretic Charges of Collodion Particles and Anomalous Osmosis through Collodion Membranes Free from Protein.** JACQUES LOEB (*J. Gen. Physiol.*, 1922, **5**, 89—107).—If a collodion membrane separate a solution of a salt at a definite $P_H$ from pure water, it is found that at $P_H 3$ the rate of diffusion of the water into the salt solution is normal, and is determined almost entirely by osmotic forces. If, however, the $P_H$ be increased, "anomalous osmosis" is obtained. Measurements have been made of the potential difference between the salt solutions and pure water, and also of that between collodion particles and such salt solutions. It is found that the anomalous diffusion rates can be largely explained as due to the potential difference between the solutions on the two sides of the membrane, and that between the membrane and the liquid in its pores. The former potential difference appears to be due to the diffusion potential. W. O. K.

**Interpretation of the Influence of Acid on the Osmotic Pressure of Protein Solutions.** JACQUES LOEB (*J. Amer. Chem. Soc.*, 1922, **44**, 1930—1941).—The effect of adding acid to casein solutions has been investigated with regard to the changes brought about in the osmotic pressure. The results show that the addition of a little acid to isoelectric casein solutions increases the osmotic pressure until a maximum is reached, after which the addition of more acid depresses the osmotic pressure. This is explained on the basis of the dispersion hypothesis by the assumption that the addition of a little acid increases the degree of dispersion and consequently the osmotic pressure of the solution, whilst the addition of more acid diminishes the degree of dispersion and consequently the osmotic pressure. The present observations show that when osmotic equilibrium is established between a solution of casein chloride enclosed in a collodion bag and an outside aqueous solution free from protein, the hydrogen-ion concentration is always greater in the outer solution than in the casein solution. There exists a membrane potential between the casein chloride solution enclosed in a collodion bag and the surrounding

aqueous solution free from protein with which the casein solution is in osmotic equilibrium, and this membrane potential can be measured with indifferent calomel electrodes and a Compton electrometer. When this is done at 24°, it is found that the number of millivolts of the observed membrane potential is equal to 59 ($P_H$ inside $-P_H$ outside), the latter values being measured with the hydrogen electrode. This is the result to be expected if the inequality of the hydrogen-ion concentrations inside and outside the casein chloride solution at equilibrium is determined by Donnan's equation for membrane equilibria (A., *1911*, *ii*, 848). The fact that the hydrogen-ion concentration inside and outside the casein chloride solution is not the same as that of the outside free from casein chloride which is in osmotic equilibrium shows that the observed osmotic pressure of the protein chloride solution cannot be entirely due to the protein, but must be partly due to the difference in the concentration of the crystalloid ions, hydrogen and chloride, in the inside and outside solution. It is therefore necessary to correct the observed osmotic pressure of a protein chloride solution for this difference of concentration of the hydrogen and chloride ions on the opposite sides of the membrane on the basis of the Donnan equilibrium. The method of evaluating this correction is demonstrated. When this evaluation is made, it is found that within the limit of accuracy of the observations and calculations the entire effect of the hydrogen-ion concentration on the osmotic pressure of the casein chloride solution is covered by the correction required and that there is little if anything left for the dispersion hypothesis to explain. This is in keeping with the conclusion previously drawn by the author, that the influence of electrolytes on the osmotic pressure of protein solutions is entirely, or almost entirely, the consequence of the difference in the concentration of crystalloid ions inside the protein solutions and the outside aqueous solutions at equilibrium, this difference being caused by the establishment of a membrane equilibrium. J. F. S.

**Selective Solvent Action by the Constituents of Aqueous Alcohol.** ROBERT WRIGHT (T., 1922, **121**, 2251—2256).

**Variations in the Solubility of a Compound in Presence of Other Compounds. I. Water–Phenol–Diphenols.** P. LEONE and E. ANGELESCU (*Gazzetta*, 1922, **52**, ii, 61—74).—The critical solubility temperature for the system water–phenol is raised by addition of naphthalene, benzophenone, calcium chloride, benzoic acid, tartaric acid, etc., lowered by addition of succinic acid, sodium oleate, or mercuric cyanide, and first raised and then lowered by increasing proportions of acetone. The addition to this system of resorcinol, quinol, or catechol produces marked increase in the reciprocal solubility and a considerable lowering of the critical temperature. Thus, the compositions of the two layers formed at any temperature in a water–phenol mixture gradually approach one another on addition of a dihydroxybenzene and, for a certain concentration of the latter, become equal. The critical temperature of the system is 66·6°; Rothmund (A., 1898,

ii, 503) found a rather higher temperature. The results obtained are given both graphically and in tabular form. T. H. P.

**Variations in the Solubility of a Compound in Presence of Other Compounds. II. Water–Epichlorohydrin–Acetic Acid.** P. LEONE and M. BENELLI (*Gazzetta*, 1922, **52**, ii, 75—86; cf. preceding abstract).—The reciprocal solubilities of water and epichlorohydrin increase as the temperature is raised, but the critical solution temperature cannot be ascertained since chemical reaction occurs at temperatures above 80°. The authors have measured the reciprocal solubilities at different temperatures and also the depressions of the temperature of saturation by addition of varying proportions of acetic acid, which is miscible in all proportions with both water and epichlorohydrin. T. H. P.

**Electronic Structures of Crystals. I.** MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1922, **44**, 1841—1850).—A theoretical paper in which the author shows how the Lewis hypothesis of atomic and molecular structures (A., 1916, ii, 310) may be applied to ascertain the relative position of electrons and electronic groups in crystals for which the atomic arrangements are known from *X*-ray investigation. It is shown that the valency electrons, in the crystals discussed, tend to form complete shells round each atomic kernel, each shell consisting of four or six electron pairs. Except for the elements of the first series of the periodic table, these pairs tend to be opposite to the faces of the kernel polyhedra. The atoms are held together by single bonds, each of which is a valency pair in the shell of two atoms and on or near the centre line between them, or by double bonds in each of which there are two electron pairs common to two atoms; the latter case obtains between the carbon and oxygen, and the nitrogen and oxygen in carbonates and nitrates, respectively. There are isolated pairs, that is pairs not acting as bonds in arsenic, antimony, bismuth, and quartz. From the point of view of the foregoing statements, the following crystals have been discussed with regard to their electronic structure: diamond, silicon, germanium, grey tin, zinc sulphide (cubic and hexagonal), cuprous chloride, bromide and iodide, silver iodide (cubic and hexagonal), zinc oxide, cadmium sulphide, carborundum, chalcopyrite, marcasite, hauerite, iron-nickel sulphide, arsenoferrite, loellingite, smaltite, safflorite, cloanthite, rammelsbergite, cobaltite, willyamite, gersdorffite, wolfachite, ullmanite, kallilite, arsenopyrite, glaucodotite, arsenic, antimony, bismuth, quartz, calcite, aragonite, carhonates of calcium, magnesium, iron (ferrous), manganese, zinc, strontium, barium, and lead, and several mixed carbonates of the above-named metals, and sodium and potassium nitrate. J. F. S.

**The Effect of Scratching the Wall of a Vessel with a Glass Rod.** L. DEDE (*Z. Elektrochem.*, 1922, **28**, 364—365). ROBERT FRICKE (*ibid.*, 365—366).—The first author criticises Fricke's explanation (*ibid.*, 244) of the manner in which crystallisation of a solution or liquid is started when the wall of the containing vessel

s rubbed with a glass rod, namely, that detached particles of glass ct as nuclei. The view is put forward that the phenomenon is lectrostatic in character, and experiments with ammonium magnesium phosphate are described supporting this view. Fricke eplies, criticising Dede's experiments and maintaining his opinion.

E. H. R.

**Crystallisation and Proteins.** ÉMILE CAVAZZANI (*Arch. internat. physiol.*, 1921, **18**, 446—450; from *Chem. Zentr.*, 1922, , 1214).—The crystallisation of ammonium chloride from saturated solutions is prevented by 0·05% of egg-albumin, or by 0·2—0·5% of gum arabic. G. W. R.

**An Electron Theory of Solids.** (SIR) J. J. THOMSON (*J. Franklin Inst.*, 1922, **194**, 281—289).—A theoretical paper giving a summary of the author's theory of the solid state (cf. this vol., ii, 252, 355). The potential energy of atoms in the crystals of the elements and the bulk moduli have been calculated, on the assumption that the attractive force between the atoms and nuclei varies as the inverse cube of the distance. The values for the uni-, bi-, and ter-valent elements are in absolute agreement with the experimental values of Richards. The excess of energy in the surface, the surface tension, has been deduced, and it is shown that this is proportional to $K^{\frac{2}{3}}$, where $K$ is the bulk modulus, a relation due to Richards. The calculation of the potential energy of the atoms in chemical compounds is complicated by the unequal distributions of the electrons about the atoms, but the numbers obtained for the bulk moduli are a useful guide to the distribution of the electrons in the crystal. W. E. G.

**Hardness of Solid Substances and its Relationship to Chemical Constitution.** A. REIS and L. ZIMMERMANN (*Z. physikal. Chem.*, 1922, **102**, 298—358).—The method of determining hardness by Marten's sclerometric method has been investigated in connexion with a large number of substances of different types, including very soft substances which exhibit a scratch of 10 $\mu$ in width when a load of only 1 gram is applied to the needle and shown to be trustworthy for this type of investigation. Experiments on the scratching of ninety crystals by one another yield results which on the whole are in agreement with those obtained by the foregoing method. The eroding action of a moving liquid on solid surfaces has been investigated and by using a stream of mercury from narrow nozzles it has been found possible to obtain trustworthy results on the resistance to erosion of solid substances. It is shown that the hardness and the resistance to erosion for the larger number of the substances examined (about one hundred and eighty) are parallel, but that the numerical value of the resistance to erosion, measured as time required for the removal of the same amount of material, increases much more than the hardness. The hardness depends on the particular crystal face employed, and on the direction of the scratch, whereas no such dependence could be observed in the erosion experiments. The relationship

between the hardness, crystal structure, and chemical constitutio has been investigated for a large number of substances of all type A general connexion is shown to exist on the basis of the classifi ation of crystal lattices according to the strength and spacial pa tition of the forces of attraction between the atoms. In the cas of those salts with lattices which are maintained by the electr static attractions of the ions, it is shown that generally the charg and distances between the ions are determinative of the hardnes In the case of compounds which have not the nature of salts, th hardness runs parallel with the strength of the residual affiniti which the molecules exert outwardly. In keeping with the gener chemical experience and with the tendency to association, it i shown from the hardness measurements that the residual affinit is smallest in the case of the hydrocarbons and increases mo strongly under the influence of hydroxyl, carboxyl, and cyanoge groups. In the case of mixed crystals, it is shown that the mixtu is harder than the mean of the components and in some cases hard than the harder component. The hardness of compressed pastill has been compared with that of crystals of the same substance and the two values are shown to be very nearly equal. A numbe of methods of producing large crystals have been investigate and it is shown that the tendency of substances to form larg crystals is to a certain extent a function of the chemical constitutio and is often parallel with the hardness. J. F. S.

**The Increase in the Size of Grain of Metallic Bodies (no previously Worked in the Cold) Formed from Powdere Material by Pressure or Sintering.** F. SAUERWALD (*Z. anorg Chem.*, 1922, **122**, 277—294).—The application of pressure di not increase the size of the grain; nor does this occur at moderat temperatures, but at higher temperatures an increase in granula size was observed in the case of iron, nickel, cobalt, tungsten, an copper. This limiting temperature could be fixed within 100° and an increase of temperature beyond this limit resulted in rapid increase in the size of the grains. This limiting temperatu is independent of the pressure applied in compressing the powde and has a characteristic value for each metal. Increase in th size of grains was not observed in the cases of zinc and aluminium These results are discussed in the light of Tammann's new theor of crystallisation (A., 1921, ii, 172). W. T.

**The Influence of Electrolytes on the Cataphoretic Charg of Colloidal Particles and the Stability of their Suspension I. Experiments with Collodion Particles.** JACQUES LOE (*J. Gen. Physiol.*, 1922, **5**, 109—126).—The potential differenc between collodion particles and the aqueous solution in whic they are suspended has been determined by measuring the mobilit of the particles under a given potential gradient. It is found tha the influence of acid and of alkali and of most salts is to cause th negative charge on the collodion particle to increase to a maximu and then to decrease with increasing concentration of the solution

A tervalent kation, however (for example, in the case of lanthanum chloride), may cause a steady decrease in the charge and even reverse it. The effects of hydrochloric acid, sodium hydroxide, lithium chloride, sodium chloride, and potassium chloride are very similar. If the $P_H$ of the solution be varied, the variation of the charge with changing concentration of salt in the solution remains similar.

When the potential difference between the particles and the solution is reduced below a certain critical value, about 16 millivolts, the suspension of colloidal particles becomes unstable, and precipitation occurs. W. O. K.

**Elasticity of Purified Gelatin Jellies as a Function of the Hydrogen-ion Concentration.** S. E. SHEPPARD, S. S. SWEET, and ANBER J. BENEDICT (*J. Amer. Chem. Soc.*, 1922, **44**, 1857—1866).—The rigidity and hydrogen-ion concentration of demineralised gelatin jellies, which are free from products of hydrolysis, has been determined for 4, 5, 7, and 10% jellies. The effect on the rigidity of the addition of 0·001% to 0·10% of alum to the above-named jellies has also been investigated. It is shown that except at very high ($P_H > 2$) and very low ($P_H < 11$) hydrogen-ion concentrations, the rigidity does not vary rapidly with changes of the hydrogen-ion concentration, the maximum being at $P_H$= 7—9. The addition of quantities of aluminium equivalent to 0·01—0·1% of alumina based on the dry gelatin produced considerable changes in the rigidity–$P_H$ curve, and markedly increased the rigidity. These results are discussed in connexion with the theory of the viscosity and elasticity of gelatin. A misleading statement on Poisson's ratio for gelatin jellies in a previous paper (A., 1921, ii, 311), and also in the literature, has been corrected.
J. F. S.

**The Ultra-filtration of Soap Solutions: Sodium Oleate and Potassium Laurate.** JAMES WILLIAM MCBAIN and WILLIAM JOB JENKINS (T., 1922, **121**, 2325—2344).

**The Reversibility of the Reaction between Nitrogen, Carbon, and Sodium Carbonate.** CHRISTOPHER KELK INGOLD and DANIEL WILSON (T., 1922, **121**, 2278—2286).

**The Ammonium Carbonate–Carbamate Equilibrium.** CARL FAURHOLT (*Z. anorg. Chem.*, 1922, **121**, 132—134).—A reply to Wegscheider's theoretical paper (this vol., ii, 376). The author shows that his results for the above equilibrium are in fair agreement with those obtained by Burrows and Lewis and by Fenton. The author also shows that the conclusions of Wegscheider (A., 1916, ii, 617) are incorrect, because the latter found that carbamic acid was very weak and the ammonium salt completely hydrolysed in aqueous solution. The present author carried out colorimetric hydrogen-ion estimations and found that the ammonium salt is not hydrolysed to any appreciable extent. W. T.

**Equilibrium in the System Potassium Chlorate, Potassium Nitrate, and Water at 25°.** SHIGERU TODA (*J. Chem. Soc. Japan*, 1922, **43**, 320—328; *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1921, **4**, 377—382).—The equilibrium in the system potassium chlorate, potassium nitrate, and water at 25° has been studied. The solubility of potassium chlorate at 25° is 7·745 grams in 100 grams of solution or 8·395 grams in 100 grams of water, and that of potassium nitrate is 27·24 grams in 100 grams of solution or 37·44 grams in 100 grams of water. At 25°, potassium chlorate forms a solid solution with potassium nitrate taking up the latter to the extent of 14·37 molar %, whilst the nitrate takes up none of the chlorate. K. K.

**Equilibrium in the System Copper Sulphate, Ammonium Sulphate, Potassium Sulphate, and Water at 25·0°.** RYONOSUKE HAYAMI (*Mem. Coll. Sci. Kyoto*, 1921, **4**, 359—369; *J. Chem. Soc. Japan*, 1921, **42**, 421—441).—The equilibrium diagram for the system copper sulphate, potassium sulphate, ammonium sulphate, and water at 25° has been determined, and also the relation between the composition of the aqueous solutions and that of the solid solutions when the residue is either a mixture of $CuSO_4,5H_2O$ and $CuSO_4,(NH_4,K)_2SO_4,6H_2O$ or a mixture of $(NH_4,K)_2SO_4$ and $CuSO_4,(NH_4,K)_2SO_4,6H_2O$. J. S. G. T.

**Dynamics of the Formation of Nitriles from Acid-anhydrides and Amides. II. Kinetic Study of the Reaction between Acetamide and Acetic Anhydride, using Phase Rule Methods.** ROBERT KREMANN, ALFRED ZOFF, and VICTOR OSWALD (*Monatsh.*, 1922, **43**, 139—144).—The reaction: acetamide+acetic anhydride $\rightleftharpoons$ acetonitrile+2 acetic acid, is followed kinetically, and shown to reach an equilibrium corresponding with 83% conversion (from left to right in the sense of the above scheme) at 98°, and with 87% conversion at 78°.

The method consisted in taking the freezing points of mixtures of the components which had been heated at the required temperature for different lengths of time. The percentage compositions were then read from an experimentally determined curve of the freezing points of mixtures of the two systems involved in the reversible reaction. C. K. I.

**Dynamics of the Formation of Nitriles from Acid-anhydrides and Amides. III. Reaction between Benzamide and Acetic Anhydride.** ROBERT KREMANN, WILHELM RÖSLER, and WILHELM PENKNER (*Monatsh.*, 1922, **43**, 145—159).—Two side reactions take place when equimolecular quantities of acetic anhydride and benzamide are heated together:

$$C_6H_5\cdot CO\cdot NH_2+(CH_3\cdot CO)_2O \rightarrow C_6H_5\cdot CN+2CH_3\cdot CO_2H \quad (I.)$$

$$C_6H_5\cdot CO\cdot NH_2+(CH_3\cdot CO)_2O \rightarrow C_6H_5\cdot CO\cdot NH\cdot CO\cdot CH_3+CH_3\cdot CO_2H \quad (II.)$$

and in order to follow the process kinetically by the method previously employed (cf. preceding abstract) it was necessary

first to construct a ternary freezing-point diagram for the systems [$C_6H_5 \cdot CO \cdot NH_2 + (CH_3 \cdot CO)_2O$], [$C_6H_5 \cdot CN + 2CH_3 \cdot CO_2H$], and [$C_6H_5 \cdot CO \cdot NH \cdot CO \cdot CH_3 + CH_3 \cdot CO_2H$]. With the aid of this diagram the progress of the reactions is followed by a series of freezing-point determinations. The following values are deduced for the composition of the equilibrium mixture: benzamide 0·48, acetic anhydride 0·48, benzonitrile 0·14, acetylbenzoylimide 0·38, acetic acid 0·66 mol. C. K. I.

**Studies in Acidolysis. I. The Equilibrium between Acetic Acid, Trichloroacetic Acid, and their Ethyl Esters. II. The Equilibrium between Acetic Acid, Trichloroacetic Acid, and their Methyl Esters.** J. J. Sudborough and D. D. Karvé (*J. Indian Inst. Sci.*, 1922, **5**, 1—21).—As a preliminary to the study of the reaction between ethyl alcohol and a mixture of acetic and trichloroacetic acids, the equilibrium between the two acids and their ethyl esters was examined at 30°. The equilibrium constant of the reaction $CH_3 \cdot CO_2Et + CCl_3 \cdot CO_2H \rightleftharpoons CH_3 \cdot CO_2H + CCl_3 \cdot CO_2Et$ was found to be equal to unity, and the same result was obtained with the methyl esters. It follows that the relative affinities of the methoxy- and ethoxy-residues for acetyl and trichloroacetyl are practically identical, in spite of the difference between the dissociation constants of the two acids. In the absence of a catalyst the reaction $CH_3 \cdot CO_2Et + CCl_3 \cdot CO_2H \longrightarrow CH_3 \cdot CO_2H + CCl_3 \cdot CO_2Et$ and the reverse reaction proceed very slowly at 30°, the time required for the attainment of equilibrium being 1200—1400 hours. The velocity constants in both directions are equal, the value of $k/V$ being 0·00039, where $k/V = 1/2A_1t \log A_1/A_1 - 2x$. In this expression, $V_1$=volume of 1000 grams of the mixture, $A_1$=the number of gram-mols. per 1000 grams, and $x$ the number of molecules which have reacted after $t$ hours. With the methyl esters, the reaction is still slower, and $k/V = 0 \cdot 000097$. E. H. R.

**The Ignition of Gases. II. Ignition by a Heated Surface. Mixtures of Methane and Air.** Walter Mason and Richard Vernon Wheeler (T., 1922, **121**, 2079—2091).

**The Explosions of Varieties of Organic Dust. Experimental Investigation of the Simple Case of Sugar Dust.** P. Beyersdorfer (*Ber.*, 1922, **55**, [*B*], 2568—2596).—The experiments consist in a thermal and an electrical investigation of the causes leading to the exploding of mixtures of very finely divided sucrose and air.

The explosion chamber consists of a glass vessel of about 600 c.c. capacity which is suspended symmetrically in a copper pot surrounded by an asbestos mantle and heated from below by a Franke burner. The vessel is provided with inlet and outlet tubes for gases and at its centre a cage of thin aluminium foil is suspended against which the sugar dust is blown through a horizontal side tube. The temperature is measured by a silver–constantan thermo-element. The sugar dust is passed through a sieve having

ten thousand meshes to the square centimetre, dried at 105°/100 mm., and preserved over concentrated sulphuric acid. The apparatus is heated to slightly above the desired temperature, and then allowed to cool to the desired extent, when the dust is blown against the foil. In this manner, the latter is the hottest part of the apparatus at the moment of the experiment.

The author defines the following terms. Ignition is a process which leads to visible combustion. Its cause may be of a dynamic, thermal, or an electrical nature. The ignition may lead to inflammation or explosion. Inflammation is a visible process of combustion which takes place throughout the material with small velocity and little change of pressure and has the power of causing further thermal ignition. Explosion is a visible process of combustion which is propagated through the material with high velocity and great change of pressure, and has the ability to ignite other combustible material by thermal action or by shock.

The author draws the following conclusions. The explosion of dusts can be caused by thermal or electrical processes. The temperature of ignition of sugar dust in air is $410 \pm 1°$, and in oxygen 371°. The presence of small quantities of ozone lowers the temperature of ignition by 3° in air and by 4° in oxygen. The temperature of ignition is dependent on the oxygen content of the gas and on the nature and thermal conductivity of the relatively inert gases which accompany the oxygen, carbon dioxide having a noticeably greater extinguishing action than nitrogen. The dependence of the temperature of ignition of sugar dust on the oxygen content of mixtures of the latter gas with nitrogen is represented graphically. The curve approaches asymptotically to the temperature axis. At a point corresponding with the presence of about 9% of oxygen, the region of ignition becomes divided into an inflammation and an explosion region. Ultimately, the thermal explosion of sugar dust is a gaseous explosion. The process occurs in two phases: (i) the gasification of sugar dust such as takes place in the case of coal, and (ii) the oxidation of the "sugar gas" until ignition sets in. [In experiments on the temperatnre of ignition of sugar dust in air in which such ignition just does not occur, a rapid initial drop of 10—15° in temperature is invariably observed (due to gasification of the sugar) followed by a rise in temperature which generally exceeds the initial temperature ultimately (due to oxidation of the gas).] The upper limit of explosion is established at 13·5 kilos. of dust per cubic metre; the lower safety limit is calculated to be 17·5 grams per cubic metre.

Sugar dust becomes positively charged when projected through the air. If it is whirled through the air, tensions of multiples of ten thousand volts may be developed. Discharge of the loaded particles in a gas may occur silently, but they have no immediate connexion with the luminosity which accompanies the process and is readily visible in the dark. This luminosity is specific for each gas, and is identical with that observed for it in an alternating field.

Sugar dust may be caused to explode in an alternating field. The phases of the electrical explosion are: (1) the formation of

ozone and nitrogen pentoxide, (2) the reaction of these substances with the most minute sugar particles, and (3) explosion as a result of this reaction in the alternating field. Sugar dust forms an aerosol with air; if this suddenly approaches the isoelectric point, a flash occurs which ignites the dust cloud.

The conclusions elucidated for sugar dust are applicable to every explosive dust whether organic or inorganic.

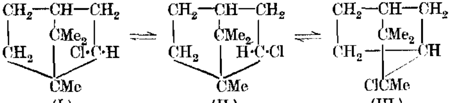
Magnetic phenomena have no influence on the occurrence of dust explosions.

The violence of a dust explosion is attributed to the adsorption of oxygen by the dust.

Triboluminesceuce cannot he regarded as a canse of sugar dust explosions. H. W.

**Michael's Addition and Separation Rule.** L. SMITH (*Z. physikal. Chem.*, 1922, **102**, 359—363).—A theoretical paper in which on the basis of the author's investigations on the velocity of the reactions $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + OH' \rightleftharpoons OH{\cdot}CH_2{\cdot}\underset{\diagdown O \diagup}{CH{\cdot}CH_2} + Cl' + H_2O$, and $OH{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}OH + OH' \rightleftharpoons OH{\cdot}CH_2{\cdot}\underset{\diagdown O \diagup}{CH{\cdot}CH_2} + Cl' + H_2O$ (A., 1920, i, 658), an attempt is made to explain Michael's addition and separation rule. This rule may be stated as follows: When two isomeric compounds may be formed from an unsaturated compound, a direct relationship exists between the relative quantities of the additive compounds produced and the velocities with which they may be reconverted into the original substance. J. F. S.

**The Equilibrium Isomerism between Bornyl Chloride, *iso*Bornyl Chloride, and Camphene Hydrochloride.** HANS MEERWEIN and KONRAD VAN EMSTER [with JACOB JOUSSEN] (*Ber.*, 1922, **55**, [*B*], 2500—2528; cf. A., 1920, i, 855).—In the molten condition and in solution, an equilibrium is established between bornyl chloride (I), *iso*bornyl chloride (II), and camphene hydrochloride (III), in accordance with the scheme:

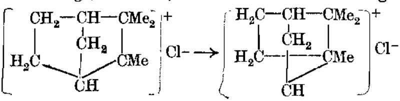


(I.) (II.) (III.)

The equilibrium is dependent on the temperature and to a slight extent on the solvent. At the atmospheric temperature, it is greatly displaced in the direction of bornyl chloride. The transformation from right to left occurs exothermally; bornyl chloride is therefore the most stable, camphene hydrochloride the most labile isomeride. With increasing temperature, the equilibrium becomes more and more displaced in favour of *iso*bornyl chloride and camphene hydrochloride. The interconversion of *iso*bornyl chloride and camphene hydrochloride takes place readily at the atmospheric temperature, whereas the transformation of bornyl

chloride into *iso*bornyl chloride occurs with greater difficulty an only at a more elevated temperature.

The velocity of the conversion of camphene hydrochloride int *iso*bornyl chloride at 20° or 40° has been examined in the followin solvents: cresol, sulphur dioxide, nitromethane, acetonitrile, nitro benzene, benzonitrile, anisole, bromobenzene, ethyl bromide, chloro bonzene, benzene, light petroleum, and ether. The rate of chang is enormously influenced by the solvent. In cresol, it occurs s rapidly that it is complete almost as soon as the camphene hydro chloride has passed into solution; ether, at the other end of th scale, acts practically as a stabilising agent towards camphen hydrochloride. The transformation is a unimolecular change. I general, the values of *k* exhibit a decreasing tendency during th course of an experiment, which is due to the partial dissociation o camphene hydrochloride in solution into camphene and hydroge chloride and the catalytic acceleration of the transformation b the latter; with decreasing content of camphene hydrochloride the concentration of the hydrogen chloride also diminishes and th rate of change becomes smaller. The results indicate that th conversion of camphene hydrochloride into *iso*bornyl chloride i due to an actual, intramolecular atomic displacement and canno be explained by elimination and re-addition of hydrogen chloride An intimate connexion is obvious between the dielectric constan of the solvent and its influence on the rate of conversion of camphen hydrochloride into *iso*bornyl chloride, the latter being greatest i strongly ionising solvents (nitromethane and acetonitrile) an smallest in non-ionising solvents (benzene, ether, light petroleum From this it appears that the velocity of the change depends on th degree of the electrolytic dissociation of camphene hydrochlorid and that the conversion only occurs subsequently to ionisatior The change, therefore, consists not in a wandering of the chlorin atom, but i a rearrange ment of th cation in ac cordance wit the annexe



scheme, whereby the more strongly ionised camphene hydro chloride passes into the less strongly ionised *iso*bornyl chloride A perfect parallelism between rate of change and dielectri constant of the solvent is not observed, exceptions being en countered in the cases of cresol, sulphur dioxide, and anisole on the one hand, and of ether on the other. Precisely these solvent have an anomalous action towards triphenylmethyl chloride, an it seems probable that their effect can be explained in a uniform manner, and that phenol, sulphur dioxide, and (to a less extent anisole form complex compounds with camphene hydrochloride i which the mobility of the chlorine atom is increased or the ionisatio of camphene hydrochloride occurs to a greater degree. Th influence of complex formation on the ionisation and therefore o the rate of transformation of camphene hydrochloride is furthe

lustrated by the catalytic acceleration of the change by the alogen acids, antimony pentachloride, stannic chloride, ferric hloride, mercuric chloride, and antimony trichloride (all of which ield additive compounds with triphenylmethyl chloride), whereas hosphorus trichloride and silicon tetrachloride, which show no endency to complex formation, are inactive. In the presence of atalysts, the change is unimolecular, and the constancy of $k$ is ıore satisfactory than in their absence, since the effect of the ydrogen chloride (see above) is of relatively less importance.

The influence of the solvent on the degree of ionisation of amphene hydrochloride is also observed in the alcoholysis of this ubstance. The conversion of camphene hydrochloride into camph-ne hydrate methyl ether by methyl alcohol has been examined inetically in the presence of nitromethane, acetonitrile, nitro-enzene, benzonitrile, anisole, bromobenzene, chlorobenzene, benz-ne, ethyl bromide, pyridine, and ether and it is found that the ffect of the solvents is approximately the same as that observed ı the conversion of camphene hydrochloride into *iso*bornyl chloride. 'he analogy between triphenylmethyl chloride and camphene ydrochloride is illustrated further by a study of the alcoholysis f the former by amyl alcohol in the presence of nitrobenzene, enzonitrile, bromobenzene, chlorobenzene, anisole, ethyl bromide, enzene, pyridine, and ether, and the complete parallelism thus stablished justifies the assumption of the ionisation of camphene ydrochloride which cannot be measured directly on account of he ease with which it is converted into *iso*bornyl chloride in all olvents which are suitable for measurements of conductivity.

Unfortunately, it is not possible to measure the rate of the reverse ransformation of *iso*bornyl chloride into camphene hydrochloride, ut it is shown to be subject to the same catalytic influences by bservation on the rate of decomposition of *iso*bornyl chloride into amphene or camphene hydrate and hydrogen chloride under iffering conditions, this decomposition being consequent on the ransformation of *iso*bornyl chloride into camphene hydrochloride.

The mutual transformation of *iso*bornyl and bornyl chlorides akes place with much greater difficulty and in non-ionising solvents ı the absence of catalysts is extremely slow at 130°. In cresol, ulphur dioxide, or chlorobenzene in the presence of stannic chloride, he change occurs with considerable rapidity at 70°, but the con-litions are unsuitable for physico-chemical examination.

The authors have previously described (*loc. cit.*) the isolation f "true" pinene hydrochloride. The compound had been btained previously in 1914 by Aschan (cf. A., 1921, i, 795), whose vork, however, was not generally accessible until recently. It has ıow been obtained in the crystalline condition (although not quite ree from bornyl chloride) by the action of hydrogen chloride on ι dilute solution of pinene in light petroleum at −60°. It is nstantly decomposed by water and alcohol, and can be titrated n alcoholic solution in the same manner as hydrochloric acid. :t resembles camphene hydrochloride in that its solutions can be greatly stabilised by the addition of ether.

The estimation of camphene hydrochloride, *iso*bornyl chloride, and free hydrogen chloride in their solutions is effected in the following manner. Camphene hydrochloride is determined by adding an excess of $N/5$-absolute alcoholic sodium ethoxide to the solution together with methyl alcohol, and titrating the excess of alkoxide after the mixture has been preserved for an hour at 20° with $N/10$-alcoholic hydrogen chloride in the presence of phenolphthalein as indicator. *iso*Bornyl chloride is estimated by boiling the mixture for an hour with $N/5$-alcoholic potassium hydroxide solution, with the addition of a little water. Free hydrogen chloride in the presence of camphene hydrochloride is estimated by taking advantage of the observation that the dissociation of the latter can be delayed to such an extent by the addition of ether that the free acid can be titrated with sodium ethoxide solution in the presence of iodoeosin as indicator.

Camphene hydrochloride is prepared by treating a solution of camphene in ether with hydrogen chloride and filtration of the product with exclusion of atmospheric moisture; the material, when most carefully prepared in this manner, contains about 9—10% of *iso*bornyl chloride. A somewhat purer product (containing 93·3% of camphene hydrochloride) can be secured by using light petroleum as solvent, in which, however, the addition of the halogen acid occurs very slowly. *iso*Bornyl chloride is obtained by saturating a solution of camphene in ethyl bromide with hydrogen chloride at 10—20°, heating the mixture uninterruptedly under a reflux condenser during six days at 55°, removing the solvent and crystallising the residue from amyl alcohol. It has m. p. 161·5°, and contains 99·6% of pure *iso*bornyl chloride; the presence of camphene hydrochloride cannot be detected. H. W.

**The Velocity of Reaction in Mixed Solvents. III. The Influence of Temperature on the Velocity of Saponification of Esters.** HAMILTON McCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and RICHARD HARDCASTLE SETTLE (T., 1922, **121** 2308—2318).

**Rate of Hydrolysis of Wheat Gliadin.** HUBERT BRADFORD VICKERY (*J. Biol. Chem.*, 1922, **53**, 495—511).—Results are given of a large number of experiments in which measurements were made of the rate of hydrolysis of gliadin by acids of various concentrations and also by alkalis. Hydrolysis both of the amide nitrogen and of the peptide linkings proceeds more rapidly the greater the concentration of the acid. In the early stages, alkalis are more effective than acids. Owing to secondary decompositions however, considerably larger quantities of ammonia are liberated by alkalis than by acids. Hydrolysis is more rapid with barium hydroxide than with sodium hydroxide of equivalent concentration. E. S.

**Influence of the Catalyst on the Thermodynamic Quantities Regulating the Velocity of a Reaction.** E. VAN THIEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 199—209).—After a theo

retical discussion of the velocity of chemical reactions in which the hypotheses of Trautz, Lewis, Scheffer, and Marcelin are considered, it is shown that the hypotheses of Trautz and Lewis demand that a reaction which is strongly catalysed shall have a smaller temperature coefficient than the same reaction uncatalysed or weakly catalysed, whilst Scheffer's hypothesis shows that a catalysed reaction can have a temperature coefficient and an energy increment which are greater than those of the uncatalysed reaction. An attempt has been made to decide between these two hypotheses by means of measurements of the rate of acetylation of diphenylamine at 0°, 20°, 30°, 40°, and 50° both without a catalyst and in the presence of *p*-bromobenzenesulphonic acid or *p*-toluenesulphonic acid as catalyst. The results of these experiments show that Scheffer's hypothesis is in keeping with the facts. J. F. S.

**Dislocation Theory of Catalysis.** J. Böeseken (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 210—215).—A theoretical paper in which the author discusses the mechanism of catalysis. He starts from the idea that ideal catalysts are those which are not temporarily fixed in intermediate compounds and so withdrawn from the reaction mass. Real catalysis is the interaction between the catalyst and the molecules which has nothing to do with the formation of a compound. This interaction is termed a *dislocation*, and may be regarded as consisting of a change in the paths of the electrons. The hypothesis is considered in the case of the photo-oxidation of alcohols in the presence of *p*-benzophenone and oxygen. In this case, the author has shown (A., 1921, ii, 500) that above a certain concentration of the ketone the velocity is independent of this concentration, and, further, it is proportional to the square of the intensity of the light and to the concentration of the alcohol, which is explained as follows: The ketone absorbs part of the light and is activated by it, the quantity of activated ketone is $I(1-e^{-kcd})$, where $k$ is the absorption coefficient, $c$ the concentration of the ketone, and $d$ the thickness of the layer. When $k$, $c$, and $d$ are large, the quantity of activated ketone becomes proportional to $I$ and independent of $c$. The whole process then is as follows: Under the influence of light a quantity of photo-ketone $kI(1-e^{-kcd})$ is formed instantaneously, this amount approaches the value $kI$, so that the first stage of the process is represented by the equation (1) ketone+light=photo-ketone, and is followed by the reaction which regulates the process. (2) photo-ketone+alcohol=(photo-ketone), alcohol; the meeting of the two molecules activates two hydrogen atoms of the alcohol and is represented by (3) (photo-ketone), alcohol $\longrightarrow$ [(photo-ketone), active alcohol]. This process which probably takes place with the velocity of light, is the real catalysis, the dislocation. The alcohol molecules are thereby brought into the condition to react according to (4) 2[(photo-ketone) active alcohol]+$O_2$=2 ketone+2 aldehyde+ $2H_2O$, which also occurs with a great velocity. The photo-ketone may be replaced by palladium, and the same type of reaction will occur and is similarly explained. This explanation demands

intimate contact between the catalyst and the reacting molecules. It is shown that Scheffer's relation of the reaction constant, $\log_e k = (E_t - E)/RT + B$ represents the thermodynamic aspect of the above hypothesis (cf. Thiel, preceding abstract). J. F. S.

**The Influencing of the Catalysis of Hydrogen Peroxide with Platinum by Röntgen Rays.** ANTON KAILAN (*Ber.*, 1922, 55, [*B*], 2492—2494).—Recalculation of the experimental results of Schwarz and Friedrich (this vol., ii, 436) show that the catalytic decomposition of concentrated hydrogen peroxide is a bimolecular action and not unimolecular as stated by these authors. In an addendum to the communication, the correctness of the criticism is recognised by Schwarz and Friedrich. H. W.

**Catalysis. XIV. The Action of Nitric Acid on Metals and an Example of a Periodic Reaction.** B. C. BANERJI and N. R. DHAR (*Z. anorg. Chem.*, 1922, **122**, 73—80).—The rate of standard solution of copper, silver, lead, nickel, brass, mint silver, and of copper-nickel alloy, in nitric acid, was studied in the presence of different salts. Ferrous salts acted as catalysts; this catalytic effect is ascribed to the nitrous acid which is formed by the action of ferrous salts on nitric acid. Ferric salts were also found to act as positive catalysts; this is due to the formation of ferrous salts by the action of the metals copper, silver, etc., on the ferric salts. Oxidising agents, for example, potassium permanganate, potassium chlorate, are negative catalysts because they prevent the formation of nitrous acid. The dissolution of a 50% copper-nickel alloy in nitric acid takes place in well-defined periods of reaction, each period being followed by a period of no reaction. W. T.

**Catalytic Action at Solid Surfaces. VIII. Action of Sodium Carbonate in Promoting the Hydrogenation of Phenol.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 21—27; cf. this vol., ii, 41).—The results of a number of experiments on the hydrogenation of phenol in the presence of nickel powder and sodium carbonate at 180° and under a pressure of hydrogen of 80 lb. per sq. inch are described. The object of the experiments was to ascertain the part played by a promoter in a catalytic change. The products of the reaction are *cyclo*hexanol 95%, some *cyclo*hexanone, with practically no unchanged phenol. The presence of sodium carbonate has an accelerating action which is dependent on the amount of carbonate present; if an excess is present the hydrogenation is retarded. The optimum amount of sodium carbonate bears no relationship to the amount of phenol present, but is closely connected with the amount of nickel catalyst employed, and in the present experiments is found to be at the point where the amount of sodium carbonate is about 25% of the weight of the nickel. The exact mechanism by which the sodium carbonate assists the hydrogenation has not been discovered, but it appears that the stimulation is not a true acceleration but the restoration of the nickel to its normal function by the suppression of a retardation, which is probably of the nature of a

poisoning of the catalyst by the phenol. It is found that the curvilinear nature of the time–absorption relationship in the absence of sodium carbonate becomes linear in the presence of this substance. This fact furnishes further evidence that the rôle of the promoter in this case is a protective one with respect to the catalyst, rendering the latter free to exert its normal functions.

J. F. S.

**Catalytic Action at Solid Surfaces. IX. Action of Copper in Promoting the Activity of Nickel Catalyst.** E. F. Armstrong and T. P. Hilditch (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 27—32; cf. preceding abstract).—It is shown that a copper–nickel catalyst may be produced in hydrogen when suitably supported compounds are heated at 180°, whereas supported nickel compounds alone are not reduced by hydrogen below 300° and not rapidly below 350—400°. It is shown that for the reduction of the nickel at this low temperature an intimate mixture of the two compounds must be used, which must be more intimate than can be obtained by mechanical mixture. Co-precipitation is not always sufficient to obtain the desired degree of intimacy, for a comparison of the activity of the catalysts with the nature of the nickel cupricarbonates from which they are produced shows that both the nickel and copper must be in the same complex molecule to obtain any degree of catalytic activity. On the basis of the foregoing, the relatively low temperature of the reduction of the nickel is explained as follows: the reduction of copper carbonate or cupric oxide is strongly exothermic, and even although the exterior temperature is only 180°, it is evident that the temperature inside the molecule must momentarily, at least, be far above the outside temperature.

J. F. S.

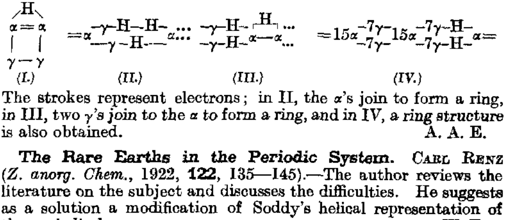
**Influence of *s*.-Trinitrobenzene on Reactions in which Arylamines are involved.** J. J. Sudborough and R. C. Shah (*J. Indian Inst. Sci.*, 1922, **5**, 29—35).—To determine whether, on account of the readiness with which polynitro-aromatic compounds form additive compounds with most of the simple arylamines, such nitro-compounds would have a catalytic influence on reactions involving aromatic amines, a number of such reactions which are readily catalysed by iodine were carried out in presence of *s*.-trinitrobenzene. The reactions studied were the methylation of aniline, formation of phenyl-α-naphthylamine from aniline and α-naphthylamine, condensation of aniline with benzophenone, the formation of thiodiphenylamine from diphenylamine and sulphur, and the acetylation of aniline. In no case had the *s*.-trinitrobenzene any catalytic influence, whilst iodine was a powerful catalyst for all except the last of these reactions.

E. H. R.

**Atoms and Electrons.** Robert N. Pease (*Nature*, 1922, **110**, 379—380).—In view of the facts (1) that the distances between the atomic centres in crystals of cerium and thorium are practically the same, the number of electrons being 58 and 90,

respectively, and (2) that in the atom of uranium (atomic volume 12·8) there are concentrated 32 more electrons than in the atom of neodymium (atomic volume 20·7), it is significant that elements of higher atomic number than uranium are not known to exist, and that most of those of immediately lower atomic number are unstable. In the case of elements of high atomic number, the electron-density must therefore be greater than in other cases, and be accompanied by a greater attractive force on the nucleus. It is suggested that periodical exertion by numbers of electrons of attractive forces on the positive nucleus in the same direction may result in the extraction of a positively charged constituent of the latter and its expulsion as an α-particle. The rate of decay would depend primarily on the stability of the nucleus, and the suggested mechanism would constitute the trigger action. A. A. E.

**Periodic Structure of Atoms and Elements.** H. NEWMAN ALLEN (*Nature*, 1922, **110**, 415).—In one of the models postulated by Crehore (A., 1921, ii, 632; this vol., ii, 438, 494), one of the particles marked 4 is also marked with a dot, evidently indicating that it has a charge $+e$ only. By calling these particles γ, it has been found possible to construct hypothetical models for a considerable number of atoms of the form indicated by the following examples representing nitrogen (I), fluorine (II or III), and uranium (IV), respectively:



(I.) (II.) (III.) (IV.)

The strokes represent electrons; in II, the α's join to form a ring, in III, two γ's join to the α to form a ring, and in IV, a ring structure is also obtained. A. A. E.

**The Rare Earths in the Periodic System.** CARL RENZ (*Z. anorg. Chem.*, 1922, **122**, 135—145).—The author reviews the literature on the subject and discusses the difficulties. He suggests as a solution a modification of Soddy's helical representation of the periodic law. W. T.

**Determination of the Molecular Weight of Substances in Alcoholic Solution from the Elevation of the Flash Point.** ROBERT WRIGHT (T., 1922, **121**, 2247—2250).

**Polar and Non-polar Valency in Organic Compounds.** W. E. GARNER (*Nature*, 1922, **110**, 543—544).—Two explanations may be given of the positive and negative relationships of groups in organic compounds: (*a*) there may be a partial transference of an electron between the group and the residue of the molecule, or (*b*) there may be a varying concentration of polar molecules in the typically non-polar substance. In the consideration of the second possibility, an equilibrium may be imagined to exist between the polar and non-polar substances which will be affected by the

temperature, nature of the solvent, etc. Thus, in those substances where the stability of the non-polar arrangement is very great, the occurrence of both forms, $\overset{-+}{AX}$ and $\overset{+-}{AX}$, will be possible, and in the presence of a suitable solvent these may give rise to the respective ions. A. A. E.

**Melting Point Tubes as Reaction Vessels.** August Fuchs (*Monatsh.*, 1922, **43**, 129—137).—Details are given for carrying out the commoner manipulations, using very small quantities of material (2—5 mg.). That satisfactory preparations and purifications can be effected by the methods indicated is proved by a record of examples actually worked out. C. K. I.

**Perforation Apparatus for the Extraction of Liquids by Liquids. Non-miscible Liquids.** Fayolle and Ch. Lormand (*Chim. et Ind.*, 1922, **8**, 273—274).—Two types of apparatus are described for the extraction of a liquid by another liquid with which it does not mix. One type is for use where the solvent is heavier than the liquid to be extracted, and the other where the solvent is the lighter of the two liquids. In either case the extraction is continuous. W. G.

**A Shaking Machine for Large Quantities of Fluid.** Hartwig Franzen (*Z. physiol. Chem.*, 1922, **122**, 86—87).—An apparatus is described suitable for stirring large amounts of lead precipitates in aqueous suspension, while treating them with carbon dioxide or hydrogen sulphide. W. O. K.

## Inorganic Chemistry.

**Vapour Pressure of Hydrogen. Determinations in the Region of Liquid Hydrogen.** H. Kamerlingh Onnes and J. Palacios Martinez (*Anal. Fis. Quim.*, 1922, **20**, 233—242).—The vapour pressures of liquid hydrogen at temperatures near its normal boiling point were measured using a helium thermometer. By interpolation, the boiling point of hydrogen at a pressure of 759·549 mm. of mercury is given as 20·35° *K* (Kelvin international scale). G. W. R.

**Spontaneous Incandescence of Substances in Atomic Hydrogen Gas.** R. W. Wood (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 1—9).—A number of experiments with very long hydrogen discharge tubes are described from which it is shown that some metals, oxides, and other substances are raised to incandescence when introduced into a stream of atomic hydrogen, the surface of the substance acting as a catalyst in bringing about the recombination of the atoms. Atomic hydrogen, practically free from molecular hydrogen, may be drawn by a pump from the central portion of a long discharge tube excited by a current of high potential. Fire

polished glass surfaces, such as the walls of a glass tube, have a comparatively feeble catalysing power whilst fractured surfaces cause the recombination of the atoms, and are strongly heated. The action of water vapour or oxygen in enhancing the Balmer spectrum, and suppressing the secondary spectrum of hydrogen, is probably due to its action on the walls of the tube, which, when dry, catalyse the atomic hydrogen as fast as it is formed by the current. The peculiar spectroscopic phenomena observed with long hydrogen tubes, described in an earlier paper (A., 1920, ii, 569) are explained. Methods are suggested for determining the physical and optical properties of atomic hydrogen gas. J. F. S.

**Evidence of the Existence of Isotopes of Chlorine.** MATAKICHI ISHINO (*Mem. Coll. Sci. Kyōtō*, 1921, **4**, 311—315).—Employing the method of positive-ray analysis, using the crossed-deflexion method devised by Thomson, the author has obtained evidence of the existence of chlorine isotopes of respective atomic weights 34 and 36, and of positively charged chlorine atoms.

J. S. G. T.

**The Decomposition of Chlorine into Atoms.** MAX TRAUTZ and WALTER STÄCKEL (*Z. anorg. Chem.*, 1922, **122**, 81—131).—The apparatus employed and methods of working are described in detail. The amount of chlorine decomposed was 1·50% at 1200°, 2·10% at 1240°, and 3·05% at 1280°. The limit of the absorption band for chlorine was found to be 390—420 $\mu\mu$. This corresponds with 67,500—73,000 cal. as the heat of decomposition according to Trautz's "approximate" equation $q_0=Ah\nu$ (A., 1918, ii, 151). The heat of decomposition of chlorine calculated from the temperature coefficient was found to be 71,000±3,000 cal. The same result was obtained by the use of the quantum theoretical constants and also by the use of Victor Meyer's vapour density measurements. With the exception of hydrogen, the heat of decomposition of the diatomic elements found experimentally agrees with the value obtained from the equation $d_0=(5{\cdot}78\times10^5/\sqrt{M})$ cal., where $M$ is the molecular weight. W. T.

**Vapour Pressure of Solid Chlorine and Bromine.** F. A. HENGLEIN, G. VON ROSENBERG, and A. MUCHLINSKI (*Z. Physik*, 1922, **11**, 1—11).—The vapour pressure of solid and liquid chlorine and solid bromine has been determined over a wide range of temperature. The following values are recorded for chlorine, 119·2° 0·0013; 126·0°, 0·0063; 133·0°, 0·028; 146·6°, 0·30; 161·1°, 2·75; 177·6°, 17·40; 194·5°, 64·40, and for bromine 177·6°, 0·0020; 210·0°, 0·26; 228·8°, 1·12; 227·0°, 1·71; and 241·1°, 6·44; the temperatures are expressed in absolute degrees and the pressures in millimetres of mercury. Vapour pressure formulæ have been deduced for both cases and have the form: $\log p=-1160/T+7773$ for liquid chlorine; $\log p=-1530/T+9950$ for solid chlorine; these formula are representative over the temperature ranges −95° to −78° and −154° to −112°, respectively, $\log p=-12150/T^{1{\cdot}368}+75030$ for solid bromine over the range −32° to

$-96°$. From the above data a number of constants have been calculated which include the following: Chlorine, m. p. 170·0° Abs.: vapour pressure at the melting point 8·9 mm., molecular heat of vaporisation at the melting point 5300 cal., heat of sublimation of solid chlorine at the melting point 6960 cal., molecular heat of fusion 1660 cal.; bromine: vapour pressure at the melting point 44·12 mm., molecular heat of sublimation at the melting point 9740 cal., specific heat of sublimation 60·91 cal., specific heat of vaporisation at the melting point 48·4 cal., molecular heat of fusion 12·5 cal. From the dissociation equilibrium of the chlorine molecule and the chemical constant as determined by Stern and Tetrode the vapour pressure of diatomic chlorine has been calculated and the chemical constant for diatomic chlorine in its normal condition has also been obtained. J. F. S.

**Physical Constants of Ozone.** E. H. RIESENFELD and G. M. SCHWAB (*Z. Physik*, 1922, **11**, 12—21; cf. this vol., ii, 637).—An account of the determination of a number of physical constants of pnre ozone which was prepared as previously described by the authors (*loc. cit.*). The following values are put on record: m. p. $-249·7°$, b. p. $-112·4°$; critical temperature, $-5°$; specific gravity at $-183°$, $1·71\pm0·1$; change of density with temperature, $1/d=a+bT+cT^2$, where $a=0·51193$, $b=0·0004559$, $c=0·000003929$; density at the boiling point, 1·46; coefficient of expansion, 0·0025; critical density, 0·537; critical pressure, 64·8 atmospheres. The authors show that neither in the gaseous nor in the liquid state is there any other molecular species present than that represented by the formula $O_3$. J. F. S.

**Solubility of Sulphur Dioxide in Suspensions of Calcium and Magnesium Hydroxides.** WM. THOMPSON SMITH and REGINALD B. PARKHURST (*J. Amer. Chem. Soc.*, 1922, **44**, 1918—1927).—The solubility of sulphur dioxide has been determined in water, milk of lime, and milk of magnesia, at partial pressures of sulphur dioxide up to 760 mm., and temperatures from 5° to 60°. All proportions of calcium and magnesium hydroxides were used in suspensions of a total alkalinity of one equivalent per litre. It is shown that the concentration of sulphur dioxide as sulphurous acid is proportional to its partial pressure. With solutions of the same alkali concentration, the percentage salting-out effect increases with, but more than in proportion to, the temperature. With solutions of constant temperature, the percentage salting-out effect increases with the alkali concentration, but is less than proportional to it. Varying proportions of calcium and magnesium hydroxide have no effect on the equilibrium concentration of sulphur dioxide as sulphurous acid. J. F. S.

**The Physico-chemical Study of the Lead Chamber Process.** MAX FORRER (*Bull. Soc. chim. Belg.*, 1922, **31**, 254—293).—A detailed description of a form of apparatus in which sulphur dioxide, nitrogen peroxide, water, oxygen, and nitrogen may be brought into contact with each other under definite conditions

of pressure, temperature, and, in the case of liquids, surface of reaction. The proportions of these substances could be varied at will. It is shown that, in such a system, the formation of sulphuric acid only occurs in presence of a liquid phase, so that the system must be heterogeneous; the formation of the acid takes place in a shorter time and the yield is increased if a liquid, either sulphuric acid or water, is present at the outset. Further, the rate at which water vapour is supplied during the course of the reaction exerts a considerable effect both on the velocity of reaction and on the concentration of the product. Under certain conditions, the acid formed may disappear, which appears to indicate that the reactions assumed to take place in the chambers are at least partly reversible. For low concentrations of the gases, there is an optimum rate of intake for water vapour: this gives the best yield and, at the same time, the most concentrated acid. As the gas concentration increases, the optimum point shifts in the direction of diminution of water supply; a curve is given showing the speed of reaction plotted against concentration of gas. The relation between these two factors is much less complex when the composition of the liquid phase is constant. The author infers from his experimental results the existence of an intermediate substance of which water is a constituent; it is, however, decomposed in presence of an excess of water. He points out that, of the series of reactions which occur, the slowest is the "limiting reaction" in that it conditions the rate of formation of the product and shows that, in practice, the reaction velocity is strongly influenced by the rate of supply of nitrogen peroxide and water, but is practically unaffected by the supply of sulphur dioxide.

An attempt is made to calculate the order of the reaction, and, for this purpose, the heterogeneity of the system and the non-equivalence of the reactants are neglected. The values obtained vary from 1·26 to 3·67. However, when the concentration of the liquid phase does not vary, the values are in the neighbourhood of 2. In the case of temperature variations which have a similar effect to that of variations in water supply, it was not found possible to obtain a coefficient in agreement with the experimental data.

H. J. E.

**Density of Atmospheric Nitrogen. A Small Anomaly in the Air of Madrid.** M. Payá and E. Moles (*Anal. Fís. Quím.*, 1922, **20**, 247—254).—The normal density of nitrogen obtained from the air of Madrid is given as 1·25681. The density of air in Madrid corresponds with a slightly higher proportion of oxygen than the normal for other places. The anomaly is attributed to the presence of higher proportion than normal of ozone and gases of the argon group.

G. W. R.

**The Reactions between Gaseous Oxides of Nitrogen and Alkaline Solutions.** A. Sanfourche (*Compt. rend.*, 1922, **175**, 469—472).—The action of oxides of nitrogen on solutions of alkali hydroxide in which the calculated proportions of nitrate and nitrite are formed only occurs if the alkali is in excess at all points

in the solution. Otherwise, reaction with the water takes place with formation of nitric acid and nitric oxide, the latter being further oxidised if oxygen is present. Moreover, if all the oxides of nitrogen are not absorbed in their first passage through the solution, this reaction with water continues in the gaseous phase with water vapour. This is shown by the formation of a nitric acid mist and by its subsequent deposition as acid dew on the upper portion of the walls of the vessel in spite of the presence of excess of alkaline solution. It is pointed out that estimation of nitrous vapours by the method of absorption in alkali hydroxide is liable to lead to considerable error and for this reason it is preferable to use sulphuric acid as the absorbent. H. J. E.

**The Solubility of Arsenic Trichloride in Concentrated Hydrochloric Acid at 100°.** W. D. Treadwell [with Ch. Mussler] (*Helv. Chim. Acta*, 1922, **5**, 818—821).—The solubility of arsenic trichloride in concentrated hydrochloric acid at 100° was determined by an indirect method which consisted in measuring the rate of volatilisation of the trichloride from the solution in a current of hydrogen chloride at 100°. From Henry's law, it follows that $\log (x_0 - x)/x_0 = -kV/V_0$, where $x$ is the quantity of trichloride volatilised by the volume $V$ of gas in a given time, $x_0$ is the quantity of trichloride originally present, $V_0$ the volume of the solution, and $k$ the solubility coefficient. Experiments showed that the value of $k$ remained constant for a considerable period of time, its mean value being 0·0233. From this it can be calculated that to volatilise 99% of the arsenic trichloride present in 100 c.c. of solution at 100° requires 19·8 litres of hydrogen chloride. From the known vapour pressure of arsenic trichloride, a litre of the vapour contains 2·34 grams. Hence the solubility in concentrated hydrochloric acid at 100° is $2{\cdot}34/k = 100{\cdot}3$ grams per litre. E. H. R.

**Boric Acid Phosphors.** Rudolf Tomaschek (*Ann. Physik*, 1922, [iv], **67**, 612—648; cf. Tiede and Wulff, this vol., ii, 245).—A number of boric acid phosphors have been prepared by the addition of phthalic anhydride, terephthalic acid, the sodium salt of fluorescein (uranin), naphthalic anhydride, and phenanthrene. The phosphorescence of these organic phosphors is in many ways simpler than that of the metal phosphors. In general, the bands of the former are all excited by the same wave-lengths of light, and owe their origin to the same phosphorescence centre. Thus the three mercury lines, 365·4, 313, and 253·6 $\mu\mu$, all appear to excite the four components of the band of the phenanthrene-phosphor. On the other hand, the different bands of the metal phosphors are excited independently. The relative intensities of the components of the bands of the boric acid substances may change with temperature; the uranin-phosphor emits a yellow light at −70°, but, when heated on metal foil, this radiation rapidly changes into a bluish-green phosphorescence. In opposition to the heavy metal phosphors, the duration and intensity of the emitted light are influenced only slightly by changes in temperature, being, in many

*cases, the same at the temperature of liquid air as at the ordinary* temperature. Neither can the phosphorescence be extinguished by exposure to red light. Phenanthrene-phosphor is especially sensitive to light, and it is shown that the decolorisation which occurs is not in any way the cause of the phosphorescence, as suggested by Perrin. The wave-lengths of the absorption bands of the transparent phosphor frequently coincide with those of the exciting radiation, and in the case of phenanthrene, correspondence is found to occur between the fluorescence bands and the absorption bands in the ultra-violet. The duration of the phosphorescence for organic boric acid phosphors is about one minute, and this comparatively short period points to the presence of very small centres; this is supported by the difficulty of fully exciting these centres. When the terephthalic acid phosphor is fully excited by an intense beam of light, the larger portion of the total phosphorescence takes place within the first second, so that the centres are mainly of very short duration. The centres do not all possess the same duration. The $1/L$ curves indicate that a bimolecular chemical reaction is not the cause of the phosphorescence, which can *be explained satisfactorily on the assumption of a photo*electric process. Three kinds of emission take place, phosphorescence, fluorescence, and an emission in the ultra-violet. The conclusion is drawn that the fields of force are almost exclusively in the interior of the organic molecules. W. E. G.

**Borates. The System $(NH_4)_2O$–$B_2O_3$–$H_2O$. Temperature–Concentration Diagram.** U. Sborgi and L. Ferri (*Mem. Accad. Lincei*, 1922, [v], **13**, 570—591).—The results previously obtained (A., 1913, ii, 213, 318; 1915, ii, 686; this vol., ii, 568) are collected. T. H. P.

**The Modifications of Silicon. II. Silicon from Copper Silicide.** Wilhelm Manchot and Herbert Funk (*Z. anorg. Chem.*, 1922, **122**, 22—26).—Specimens of silicon obtained from a copper silicide regulus have been studied; the results were similar to those obtained by the authors when employing aluminium and *silver reguli (this vol., ii, 286).* Conditions which favour the formation of crystals produce silicon which reacted but slowly with hydrofluoric acid. Crystalline silicon very soluble in this acid could not be obtained. W. T.

**Alkali Iodides.** L. W. Winkler (*Pharm. Zentr.-h.*, 1922, **63**, 386—387).—Analyses of samples of commercial potassium iodide and sodium iodide showed that these substances have a high degree of purity. The respective quantities of iodide found corresponded with 98·6 to 99·6% of potassium iodide and with 97·0 to 99·9% of sodium iodide. W. P. S.

**Composition of the Liquid Phases in a Univariant System, Liquid–Liquid–Vapour, for Mixtures of Sodium and Ammonia.** Charles A. Kraus and Walter W. Lucasse (*J. Amer. Chem. Soc.*, 1922, **44**, 1949—1953).—In an earlier paper (A., 1907, ii), it has been shown that at low temperatures concentrated

solutions of sodium in liquid ammonia separate into two liquid phases which have an upper critical end-point at about $-45°$. The concentrations of these liquid phases have now been determined by electrical conductivity measurements and it has been found that the upper critical end-point lies at $-41·6°$ and at a composition of 4·15 atom % of sodium. The phase relations in the system sodium–ammonia are briefly discussed. J. F. S.

**Nature of the Complexes formed between Sodium and Tellurium in Liquid Ammonia.** CHARLES A. KRAUS and C. Y. CHIU (*J. Amer. Chem. Soc.*, 1922, **44**, 1999—2008).—The reaction between sodium and tellurium in liquid ammonia has been investigated and the composition of the resulting solutions has been determined under various conditions. The initial compound formed is normal sodium telluride of the formula $Na_2Te$. In equilibrium with the normal telluride, the complex in solution has a composition corresponding with the formula $Na_2Te_2$. In equilibrium with free tellurium the solution has a composition which varies as a function of the concentration. The maximum amount of tellurium present corresponds approximately with the formula $Na_2Te_4$. J. F. S.

**Crystal Structure of Silver Molybdate.** RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1994—1998).—Making use of the data obtained from the reflection spectra and Laue photographs of silver molybdate, the crystal structure of this substance has been shown to be the same as that of the spinels and magnetite. The length of the side of the unit cube, which contains eight molecules, is 9·26 Å.U., and the parameter defining the position of the oxygen atoms is very close to 3/8. The distance between molybdenum and adjacent oxygen atoms is 2·00 Å., between silver and the nearest oxygen atom 2·31 Å., and between the nearest molybdenum atom and silver 4·02 Å. J. F. S.

**The Dissociation of the Chlorides of Bivalent Metals in Aqueous Solution.** A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1922, **28**, 387—389).—In a previous paper it was shown from a study of the basic exchange between copper salts in solution and permutite that the copper salt solution, even at high dilutions, contains complex kations (this vol., ii, 504). The investigation has now been extended to salts of barium, strontium, calcium, cadmium, manganese, cobalt, and nickel, using the chlorides of the metals and ammonium permutite. If $a$ represents the number of equivalents of metal passing into the permutite in exchange for ammonia, and $c$ the number of equivalents of chlorine likewise disappearing from the solution, then if the metallic chloride is present in solution only in the form of $M^{\cdot\cdot}$ and $Cl'$ ions, $c=0$ and $a/c=\infty$. If, however, the ions are $MCl^{\cdot}$ and $Cl'$, the $MCl^{\cdot}$ ion passing into the permutite, $a/c=2$. If still more complex ions are formed, such as $M_2Cl_3^{\cdot}$, $a/c<2$. Applying this reasoning to the experimental results, it is found that at the highest concentrations of all the above salts, some $MCl^{\cdot}$ ions are present and,

in the cases of magnesium, nickel, and copper, still more complex ions. The first stage of dissociation into MeCl˙ and Cl′ preponderates in the case of those metals having the smallest ionic radius. At a dilution of 1·0$N$, a considerable proportion of MeCl˙ ions is found only in the case of those metals having the smallest ion radius, namely, nickel and copper. E. H. R.

**Transference of the Acid Radicle in the Solid Phase. I. Carbonates of the Alkaline Earths and Magnesium.** J. Arvid Hedvall and J. Heuberger (*Z. anorg. Chem.*, 1922, **122**, 181—187).—It was found that if the oxides of the elements considered are arranged in order of increasing basicity MgO, CaO, SrO, BaO, then the oxide of the more basic will on heating with the carbonate of the less basic element be changed into the carbonate without the evolution of gas and at a temperature well below the temperature of dissociation of the carbonate taken. The temperature of the reaction decreases and the heat effect increases with increasing difference of basicity, for example, $MgCO_3+BaO=BaCO_3+MgO+19$ cal. ($t=230°$); $SrCO_3+BaO=BaCO_3+SrO+6·14$ cal. ($t=280°$). W. T.

**The Crystal Structure of Glucinum and Glucinum Oxide.** L. W. McKeehan (*Proc. Nat. Acad. Sci.*, 1922, **8**, 270—274).—The glucinum was obtained by electrolysis of sodium glucinum fluoride, $2GlF_2,NaF$, and contained a few per cent. of glucinum oxide. The diffracting centres in the metal and its oxide lie at the points of two symmetrically interpenetrating hexagonal space lattices. For glucinum oxide, the axial ratio, $c/a=1·63$, and $a=2·696\times10^{-8}$ cm.; for glucinum, $c/a=1·58$ and $a=2·283\times10^{-8}$ cm. These values give computed densities within 1% of the best previous values. Glucinum more closely resembles magnesium, zinc, and cadmium, rather than calcium, strontium, and barium; the oxide is an analogue of zinc oxide, and the structure suggested by W. L. Bragg (A., 1920, ii, 433) for the latter substance is also possible for glucinum oxide. W. E. G.

**Physical Chemistry of the Oxides of Lead. VI. The Anodic Behaviour of Lead and Lead Dioxide.** Samuel Glasstone (T., 1922, **121**, 2091—2098).

**The Isomerism of Metallic Oxides. I. Lead Monoxide.** Malcolm Percival Applebey and Robert Douglas Reid (T., 1922, **121**, 2129—2136).

**The Hindrance of Precipitations with Hydrogen Sulphide by Neutral Chlorides.** L. Dede and P. Bonin (*Ber.*, 1922, **55**, [*B*], 2327—2331).—The action of hydrogen sulphide on a 1/1000-molar solution of lead chloride in water at 20° in the presence of hydrochloric acid and of neutral chlorides has been investigated. Precipitation of lead sulphide is completely inhibited by hydrochloric acid alone if present in a concentration of 1·4$N$. In the presence of increasing quantities of calcium, ammonium, or potass-

ium chlorides, decreasing concentrations of hydrochloric acid are sufficient to prevent precipitation entirely. In the presence of considerably smaller concentrations of hydrochloric acid, the precipitation of lead sulphide is incomplete. At higher temperatures, the effect of hydrochloric acid in the presence of neutral chlorides is still more marked. Similar results are obtained with cadmium salts, and apparently also with tin salts. The precipitation of lead sulphide is also hampered, although to a less degree, by the presence of perchloric acid. In this case, however, the addition of sodium perchlorate favours precipitation presumably by depressing the dissociation of the acid.

The precipitation of lead chromate in acetic acid solution is not quantitative in the presence of much chloride; in ammoniacal solution this is not the case. H. W.

**The Constitution of Basic Lead Salts.** R. WEINLAND and RUDOLF STROH (*Ber.*, 1922, **55**, [*B*], 2706—2718).—It has been assumed by Werner (A., 1908, ii, 42) that certain basic salts are to be regarded as aquo-salts in which the water molecules are replaced by metallic hydroxide, that is, as compounds containing a polynuclear kation; thus, atacamite, $CuCl_2,3Cu(OH)_2$, has been formulated $\left[Cu\left(<\substack{OH\\OH}>Cu\right)_3\right]Cl_2$. The presence of such ions in several forms has been established by preparative substitution in the case of lead salts. Thus, in the basic perchlorates, $[Pb_2(OH)_2](ClO_4)_2,1{\cdot}5H_2O$ (I) and $[Pb_3(OH)_4](ClO_4)_2$ (II), the perchlorate residues could be replaced by other acid radicles. The stability of the metal-ol kations is not to be compared with that of the typical metal ammines in aqueous solution, since the above basic perchlorates are to some extent decomposed into new basic salts when their solutions are diluted, so that, at any rate, a partial change has occurred in the complex. This instability is also shown by the fact that potassium ferricyanide and potassium cobalticyanide give salts with differently constituted lead kations from those obtained with alkali chlorides. The presence of such lead-ol complexes in basic lead acetates has also been established by the substitution method in the case of the basic lead acetate; one such ion is identical with that contained in the perchlorate (I).

Polynuclear lead kations are also present in the neutral lead acetate–perchlorates and lead acetate–nitrates (Weinland and Stroh, this vol., i, 981). They are distinguished from those contained in the basic salts only by containing acetato- instead of ol-bridges, thus: $[Pb_2(OH)_2](ClO_4)_2,1{\cdot}5H_2O$ and $[Pb_2(CH_3CO_2)_2](ClO_4)_2,H_2O$. Application of these considerations to lead acetate itself causes the authors to regard it as the acetate of a polynuclear lead acetato-kation. In aqueous solution, undoubtedly more than one such kation is present, since the action of perchloric acid on lead acetate in neutral and acetic acid solution yields the perchlorates of four different lead acetato-kations. It has not yet been found possible to decide which kation is present in solid lead acetate, $Pb(OAc)_2,3H_2O$.

Basic lead perchlorate (I) is readily prepared from a solution of

lead monoxide in the calculated quantity of perchloric acid; its electrical conductivity indicates that three ions are present in its solutions. It is converted by double decomposition into basic lead chloride, $[Pb_2(OH)_2]Cl_2$, a colourless powder which does not appear under the microscope to be crystalline; basic lead nitrate, $[Pb_2(OH)_2](NO_3)_2$, *basic lead dithionate*, $[Pb_2(OH)_2]S_2O_6$, lustrous leaflets and needles, and *basic lead nitroprusside*,

$$[Pb_2(OH)_2]\left[Fe^{NO}_{(CN)_5}\right],H_2O,$$

pale brownish-red cubes. With potassium ferricyanide and potassium cobalticyanide, it gives the analogously constituted *compounds*, $Pb_4(OH)_2[Fe(CN)_6](ClO_4)_3$, a brown powder, and

$$Pb_4(OH)_2[Co(CN)_6](ClO_4)_3,$$

a colourless, heavy powder.

*Basic lead perchlorate* (II), tetrahedra and octahedra, is prepared by cooling a hot solution of perchloric acid which has been saturated with lead monoxide. It is converted by double decomposition into basic lead chloride, $[Pb_3(OH)_4]Cl_2$, a yellowish-white powder; basic lead iodide, a yellow powder; basic lead nitrate, $[Pb_3(OH)_4](NO_3)_2$, a heavy, white powder, and *basic lead dithionate*, $[Pb_3(OH)_4]S_2O_6$, a colourless, crystalline precipitate. The following salts, also prepared by double decomposition, do not contain the original kation: *basic lead chromate*, $[Pb_2(OH)_2],CrO_4$, a fine, red powder; *basic lead ferricyanide-perchlorate*, $Pb_3(OH)_5[Fe(CN)_6](ClO_4)_2$, a pale brown powder which explodes violently when heated; *basic lead ferricyanide*, $Pb_5(OH)_7[Fe(CN)_6],3{\cdot}5H_2O$, a yellow powder; *basic lead cobalticyanide-perchlorate*, $Pb_5(OH)_5[Co(CN)_6](ClO_4)_2,1{\cdot}5H_2O$, a heavy, white powder; *basic lead nitroprusside-perchlorate*,

$$Pb_4(OH)_5[Fe(CN)_5NO]ClO_4,H_2O,$$

pale, brownish-red, crystalline aggregates.

Basic lead acetate is shown to contain the same kation as the perchlorate (I) by the fact that it gives by double decomposition the same basic chloride and dithionate. Concentrated solutions of the salt and potassium ferricyanide give the *salt*, $Pb_6(OH)_7[Fe(CN)_6](CH_3{\cdot}CO_2)_2,H_2O$, brownish-red crystals, whereas dilute solutions yield a dark yellow, amorphous precipitate which fairly rapidly passes into the *compound*, $Pb_4(OH)_5[Fe(CN)_6]$, garnet-red prisms (the corresponding cobalt *compound*,

$$Pb_4(OH)_5[Co(CN)_6],$$

is prepared similarly). Treatment of the ferricyanide last mentioned with dilute acetic acid leads to the formation of the salt $Pb_3(OAc)_5[Fe(CN)_6],2H_2O$, brownish-red needles. Solutions of lead acetate and sodium perchlorate give, under different conditions, the *salts*, $Pb(OAc)_2,NaClO_4$, rectangular prisms capped by pyramids at either end; $Pb_2(OAc)_3,NaClO_4,3H_2O$, colourless needles, and $Pb_4(OH)_4(ClO_4)_4,NaClO_4,3H_2O$, large, many-sided plates. H. W.

**The Complex Cuprammoniates $Cu(CN)_2,CuCN,2NH_3$; $Cu(CN)_2,4CuCN,4NH_3$; $Cu(CNS)_2,Cu(CN)_2,5CuCu,6NH_3$, and the Analytical Methods for their Identification.** F. HALLE and K. HIRSCHKO (*Z. anorg. Chem.*, 1922, **122**, 188—194).—The

above three new complex cuprammoniates have been prepared, and details are given of their analysis. W. T.

**Critical Constants of Mercury.** SOPHUS WEBER (*K. Danske Vid. Medd.*, 1920, **3**, No. 4, 1—12; from *Chem. Zentr.*, 1922, iii, 27).—From theoretical considerations, the author derives the following critical constants for mercury: $t_c$ 1450°; $d_c$ 5·0; $p_c$ 1042 atmospheres. The same value for $p_c$ is given by extrapolation at 1450° with Knudsen's vapour pressure formula. The correlation of the Trouton constants with the critical data established by Cederberg is valid for the above values. The reduced vapour pressure curve for mercury approximately coincides with the curve for hydrogen. G. W. R.

**Oxychlorides of Mercury. Equilibrium in the System Mercuric Chloride, Yellow Mercuric Oxide, and Water at 35°.** SHIGERU TODA (*J. Chem. Soc. Japan*, 1922, **43**, 312—320; *Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1921, **4**, 305—310).—The equilibrium in the system mercuric chloride, yellow mercuric oxide, and water at 35° has been studied. The solubility of mercuric chloride, 9·39 grams in 100 grams of water, and that of yellow mercuric oxide is 0·0014 gram in 100 grams of water. In the system investigated, two oxychlorides of mercury were found to exist: $HgCl_2,2HgO$, purplish-scarlet needles, and $HgCl_2,4HgO$, a brownish-yellow, amorphous substance. It is probable that the latter forms a solid solution with mercuric oxide. K. K.

**The Rare-earth Magnesium Sulphide Phosphors.** ERICH TIEDE and ARTHUR SCHLEEDE (*Ann. Physik*, 1922, [iv], **67**, 573—580).—Phosphors containing cerium, lanthanum, didymium, praseodymium, neodymium, samarium, yttrium, gadolinium, erbium, ytterbium, scandium, thorium, and zirconium were prepared by the methods previously described (Tiede and Richter, this vol., ii, 215). They were all yellow in colour and, like the phosphors of the heavy metals, this colour was destroyed by pressure. The temperature relationships, and the spectrum of the phosphorescent light of the magnesium samarium phosphor were very similar to those of the calcium samarium phosphor of Hauer and Kowalski (A., 1914, ii, 320). Cerium, didymium, praseodymium, samarium, gadolinium, and scandium gave the best phosphors in the ordinary sense of the word, although the other metals gave strong phosphorescence in the cathode ray tube. The colour of the phosphorescence ranged from orange-yellow to pale green, and the duration of the emitted light was approximately twenty minutes. The spectra differed considerably from those of the phosphors of the heavy metals, being composed of intense sharp lines and bands. The exciting light, in all cases, lay in the ultra-violet. W. E. G.

**The Separation of the Rare Earths by Basic Precipitation. IV.** WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Z. anorg. Chem.*, 1922, **122**, 311—314).—The influence of cadmium nitrate on the equilibrium between the nitrates of the rare earths and ammonia in ammonium nitrate solutions of various concen-

trations has been investigated. The conditions were the same as in previous experiments (cf. this vol., ii, 298). The presence of cadmium nitrate increased considerably the amount of rare earth kept in solution, especially lanthanum, this increase being much more marked than in the case of zinc nitrate. W. T.

**Rare Earths. III. Atomic Weight of Lanthanum.** B. S. Hopkins and F. H. Driggs (*J. Amer. Chem. Soc.*, 1922, **44**, 1927—1929).—The atomic weight of lanthanum has been determined by a comparison of lanthanum chloride with silver. The material used was the less soluble portion of the magnesium rare-earth nitrates from which the whole of the cerium had been removed by James and Pratt's method (A., 1911, ii, 935). The sparingly soluble fractions containing lanthanum and praseodymium were fractionated further as double ammonium nitrates until the first twenty fractions failed to show the faintest trace of the praseodymium absorption spectrum. Fractions 7 and 8 of this series were precipitated with hot dilute oxalic acid solution, the precipitate filtered, washed, and ignited to oxide which was dissolved in nitric acid, and the solution treated with ammonia gas to precipitate the hydroxide. The alternate precipitation as oxalate and hydroxide was repeated four times, the last two taking place in conductivity water. The final oxide was suspended in conductivity water and treated with hydrogen chloride in a quartz flask. This material showed no spectroscopic lines of any of the related elements. The solution of lanthanum chloride was dried in a quartz flask in a current of air and hydrogen chloride until crystallisation commenced, the air current was shut off, and hydrogen chloride alone passed in until, at 85°, the first five molecules of water of crystallisation had come off, then the temperature was raised to 125°, when the final molecule of water commences to come off. As soon as this evolution was complete, the temperature was raised to 325°, and kept there for an hour, after which the salt was rapidly melted over a bunsen flame and then allowed to cool. The hydrogen chloride was displaced by dry air and the material weighed. The chloride was treated with silver solution and exact equivalence between the two substances determined nephelometrically. Using the data: density, $LaCl_3$=3·947, Ag=10·5; atomic weights, Ag=107·88, Cl=35·457, it was found that 1·02450 grams $LaCl_3$ is equivalent to 1·35189 grams of silver, whence the mean atomic weight of lanthanum (10 expts.)=138·89; the extreme values being 138·84 and 138·97. This value is very close to 138·91, the value found by Baxter, Tani, and Chapin (A., 1921, ii, 454), and seems to indicate that the value 139·0 adopted by the International Atomic Weight committee is slightly too high. J. F. S.

**The Separation of the Rare Earths by Basic Precipitation. III. The Quantitative Separation of Cerium from the Other Earths.** Wilhelm Prandtl and Joseph Lösch (*Z. anorg. Chem.*, 1922, **122**, 159—166).—The separation is based on the fact that ceric hydroxide is a weak base and its salts are highly hydrolysed. Cerous nitrate mixed with the nitrates of the other rare

earths was oxidised by trinitratocobalttriammine in acid solution with quantitative precipitation of the ceric hydroxide, $Ce(NO_3)_3 + [Co(NH_3)_3(NO_3)_3] + 4H_2O = Ce(OH)_4 + Co(NO_3)_2 + 3NH_4NO_3 + HNO_3$. The formation of free acid prevents the precipitation of the other rare earths. W. T.

**Intermetallic Actions. The System Aluminium-Arsenic.** QASIM ALI MANSURI (T., 1922, **121**, 2272—2277).

**The Constitution of Aluminates.** JAROSLAV HEYROVSKY (*Chem. News*, 1922, **125**, 198—199).—In order to investigate further the monobasicity of "aluminic acid" (cf. T., 1920, **117**, 1013), cryoscopic and conductivity determinations were made on solutions of the alkaline-earth hydroxides when gradually saturated with aluminium hydroxide in the nascent condition, generated by the action of the solution on amalgamated aluminium. The regular fall in conductivity observed and the slight changes in the lowering of the freezing point show that only univalent aluminate ions exist. In contact with crystalline aluminium hydroxide, all the solutions are about 50% hydrolysed; with nascent aluminium hydroxide, the hydrolysis is only 1—1·5%. The process by which aluminium hydroxide dissolves in alkali is undoubtedly by complex-ion formation, $Al(OH)_3 + OH' \longrightarrow Al(OH)_4'$, and not, as is often stated, by sending into solution one, two, or three of its hydrogen atoms as hydrions. The hydrolysis of aluminates is therefore, on this view, not due to scarcity of hydrions, but to the incompleteness of the complex formation. G. F. M.

**The Properties of Potassium Permanganate.** G. FESTER and G. BRUDE (*Z. angew. Chem.*, 1922, **35**, 527).—Crystals of pure potassium permanganate prepared in the dark and in air free from carbon dioxide and organic matter, are brown and have a bronze, metallic lustre. The finely powdered crystals, however, show a dark violet colour. When exposed to subdued daylight and ordinary air, the surfaces of the crystals develop a violet colour in a few hours and a steel blue lustre after two days. This change is confined to the surface layer, which acts as a protective layer to the remainder of the crystal. The change is particularly rapid in an atmosphere containing mineral acid. The crystals of potassium permanganate should be described as bipyramidal rhombs rather than as prisms. Potassium permanganate oxidises paper and most other organic substances, so that the statement that it is without action on litmus paper is untrue. H. C. R.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. IV. Reduction of Permanganate by Formate in Alkaline Solutions.** JOSEF HOLLUTA (*Z. physikal. Chem.*, 1922, **102**, 276—297; cf. this vol., ii, 448, 628, 700).—A continuation of previous work. It is shown that the reduction of permanganate by formates in alkaline solution takes place in two stages which are sharply separated from one another. In the first stage, the reduction of permanganate to manganate takes place, and this is reduced to an alkali manganite in the second

stage. The first stage takes place according to the equation $2MnO_4'+HCO_2'+3OH'=2MnO_4''+CO_3''+2H_2O$, and it is shown that a disturbance occurs in the reaction at a point immediately before the completion of the reduction to manganate due to the commencement of the reduction of the manganate. The first stage is shown to be a second order reaction, inasmuch as one molecule of permanganate apparently oxidises one molecule of formate. To explain the behaviour of the manganate and the low order of the reaction it is assumed that it is not the permanganate itself which oxidises the formate, but atomic oxygen which is split off from the permanganate under the influence of the hydroxyl ions. It is further assumed that the hydroxyl ions, through the formation of an additive compound with the permanganate, act as oxygen carriers. It is shown that the above assumptions can be justified on the basis of the experiments and calculations of Sackur and Taegener (A., 1912, ii, 916). The temperature coefficient of this reaction is found to be 2·06. From the potential measurements of Sackur and Taegener (*loc. cit.*), the equilibrium constant of the reaction $2MnO_4''+2H_2O \rightleftharpoons 2MnO_2+4OH'+O_2$ is calculated to be 53·1 for 18—20°. It is shown that the presence of hydroxyl ions accelerates the reaction, the cause of which being in all probability that the hydroxyl ions affect the equilibrium pressure at which oxygen is separated from the permanganate hydroxyl ion complex.
J. F. S.

**The Diffusion of Carbon in Metals and in Mixed Crystals of Iron.** G. TAMMANN and K. SCHÖNERT (*Z. anorg. Chem.*, 1922, **122**, 27—43).—Carbon was found to diffuse into iron at 750°, whereas no diffusion into the other metals took place at 980°. In mixed crystals of iron with tungsten, molybdenum, nickel, cobalt, and manganese containing a large amount of iron, the diffusion was found to increase with the addition of the second element until a maximum was reached; the diffusion then diminished. In the cases of tungsten and molybdenum, the maxima corresponded with 0·0306 molar concentration, and the diffusion increased by 0·166; with nickel, cobalt, and manganese as added metals, the maxima required a molar concentration of 0·114, and the increase in diffusion was 0·057. The diffusion coefficients found for different pieces of iron were found to vary; this was due to the foreign matter between the crystallites.
W. T.

**Photochemical Examination of the Reaction between Ferric Salts and Iodides.** NOBUJI SASAKI (*Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1922, **5**, 315—327).—The reaction between ferric salts and iodides is retarded by exposure to sunlight or bright artificial light, whilst that between ferrous salts and free iodine is accelerated. These photochemical reactions are discussed, and are shown to follow a simple law.
W. P. S.

**System $Fe_2O_3$-$SO_3$-$H_2O$.** E. POSNJAK and H. E. MERWIN (*J. Amer. Chem. Soc.*, 1922, **44**, 1965—1994).—The system ferric oxide–sulphur trioxide–water has been investigated over the

temperature range 50—200°, by heating various mixtures of the components at various temperatures and analysing the phases produced. The following crystalline phases have been obtained: $Fe_2O_3$; $Fe_2O_3,H_2O$; $3Fe_2O_3,4SO_3,9H_2O$; $Fe_2O_3,2SO_3,H_2O$; $Fe_2O_3,2SO_3,5H_2O$; $2Fe_2O_3,5SO_3,17H_2O$; $Fe_2O_3,SO_3$ (2 forms); $Fe_2O_3,3SO_3,6H_2O$; $Fe_2O_3,3SO_3,7H_2O$; $Fe_2O_3,4SO_3,3H_2O$, and $Fe_2O_3,4SO_3,9H_2O$. The conditions under which these substances are formed, the ranges of their stability, and some of their crystallographic and optical properties have been determined. J. F. S.

**Some Poly-acids of the Elements of the Sulphur Group.** JULIUS MEYER and VALENTIN STATECZNY (*Z. anorg. Chem.*, 1922, **122**, 1—21).—The poly-acids formed by elements of the sulphur group are formulated according to the co-ordination system with a co-ordination number equal to four. The authors have succeeded in preparing the following heteropoly-acids and some of their salts: chromosulphuric acid, $H_2[CrO_3(SO_4)]$, and its potassium, sodium, ammonium, barium, strontium, and calcium salts; chromoselenic acid, $H_2[CrO_3(SeO_4)]$, together with its potassium and barium salts. Methods of preparation are given in detail. The solubilities of chromic anhydride in sulphuric and selenic acids of various concentrations were determined and a method was given for the preparation of the pure anhydride. The existence of the sulphoselenic acids, $H_2[SeO_3(SO_4)]$ and $H_2[SeO_2(SO_4)_2]$, was indicated by thermal analysis. Sulphomolybdic acid, $H_2[MoO(SO_4)_2(MoO_4)]$, was also prepared, but the corresponding selenic acid could not be isolated. Indications were obtained of the existence of chromyl-sulphuryl chloride, $CuSO_5Cl_2$. W. T.

**Experimental Attempts to Decompose Tungsten at High Temperatures.** GERALD L. WENDT and CLARENCE E. IRION (*J. Amer. Chem. Soc.*, 1922, **44**, 1887—1894).—Attempts have been made to decompose tungsten by rapidly discharging a condenser holding 30,000—45,000 volts through a tungsten wire 4 cm. long and 0·035 mm. diam., either in a vacuum or in carbon dioxide at 1 atm. pressure. In this way, momentary temperatures above 20,000° were produced in the wires which were entirely dissipated, no smoke, dust or solid residue being found after the explosion. Abundant quantities of gas were present after the explosions in a vacuum, and a spectroscopic examination of this showed the strong yellow helium line, and two red, one bright blue, and one pale violet line were also observed but have not been identified. The gas from the explosions in carbon dioxide was collected and measured, and it was found that about the same weight (mean 0·713 mg.) of tungsten yields in different experiments from 3·62 to 0·30 c.c. of gas unabsorbable by potassium hydroxide. It is pointed out that if the whole of the tungsten had been decomposed into helium the volume of gas would have been 4·0 c.c. J. F. S.

**The Hydrates of Tungsten Trioxide.** GUSTAV F. HÜTTIG and BRUNO KURRE (*Z. anorg. Chem.*, 1922, **122**, 44—50).—The

existence of hydrates of tungsten trioxide was investigated by the Hüttig tensi-eudiometer (A., 1921, ii, 195). Solutions of the pure white and yellow acids were employed, and the process of dehydration was followed. No compound was indicated in the case of the white acid, the temperature–composition curve indicating adsorption as the water content changes gradually. The dehydration of the yellow acid showed the existence of a monohydrate $WO_3,H_2O$. The authors found that at temperatures above 188° and below 76° the white acid is the more stable, whereas between 76° and 188° the yellow variety is the stable form. W. T.

**Sodium Tungstates. I.** EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 2027—2036).—Tungstates in which the basic and acidic oxides are present in the ratio 4 : 10 constitute a very definite series of salts. The sodium compound, $4Na_2O,10WO_3,23H_2O$, can be prepared by the method of Forcher and Gibbs, by passing carbon dioxide during several days through an aqueous solution of normal sodium tungstate or by the gradual addition of formic acid, until the action is distinctly acid, to a solution of normal sodium tungstate (100 grams) in water (100 c.c.). A mixture of the salts $4Na_2O,10WO_3,23H_2O$ and $5Na_2O,12WO_3,28H_2O$ is produced by the action of glacial acetic acid on a solution of sodium tungstate; the product, $9Na_2O,22WO_3,51H_2O$, appears to be a mixture of the two salts described above. The salt $4Na_2O,10WO_3,23H_2O$ forms monoclinic crystals which effloresce rapidly in dry air. It is soluble in water to the extent of 19 parts in 100 parts at atmospheric temperature; and has *d* 4·3. The following melting points are recorded for the various sodium tungstates: $Na_2O,WO_3$, 665°; $5Na_2O,12WO_3$, 705·8°; $4Na_2O,10WO_3$, 680·8°; $9Na_2O,22WO_3$, 683·3°; $Na_2O,4WO_3$, 706°. Addition of an excess of the respective metallic chlorides to a boiling aqueous solution of the salt $4Na_2O,10WO_3,23H_2O$ leads to the formation of the following compounds: *calcium* salt, $4CaO,10WO_3,25H_2O$, a white, granular powder which does not melt when heated to intense redness; the *barium* salt, $4BaO,10WO_3,22H_2O$, and the *strontium* salt, $4SrO,10WO_3,26H_2O$, white, insoluble, granular powders; the *nickel* salt, $4NiO,10WO_3,34H_2O$, a greenish-white powder; the *cobalt* salt, $4CoO,10WO_3,35H_2O$, pink granules; the *manganese* salt, $4MnO,10WO_3,30H_2O$, a colourless, granular powder. The action of a solution of the sodium salt, $4Na_2O,10WO_3,23H_2O$, towards solutions of salts of many inorganic and organic bases has been examined qualitatively. The sodium salt loses the whole of its water of crystallisation when it is strongly ignited, but when dried at 100° until constant in weight it retains six molecular proportions. It therefore appears that it may be formulated definitely as an acid salt, $4(Na_2O,WO_3),6(H_2O,WO_3),17H_2O$, and similar considerations are extended to the tungstates of other series. Confirmation of its acidic character is found in the ready neutralisation of its solutions with *N*-sodium carbonate solution and also in conductivity (J. ... periments during its neutralisation with barium hydroxide oxide-...n.

**The Binary Systems $Na_2SiO_3$–$Na_2WO_4$, $K_2SiO_3$–$K_2WO_4$, ıd $Na_2WO_4$–$K_2WO_4$.** J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 22, **122**, 175—180).—Klooster (A., 1911, ii, 111) examined the stem $Na_2WO_4$–$Na_2SiO_3$ and found no indications of a compound; e liquid salts were found to be immiscible. The present author ıs examined the viscosity and conductivity of aqueous solutions the mixture. Curves representing the results showed no maxima minima. The system $K_2WO_4$–$K_2SiO_3$ gave similar results. ıe equilibrium curve for the system $K_2WO_4$–$Na_2WO_4$ was obtained the cooling method; a minimum freezing point was found for mixture containing 80% of the sodium and 20% of the potassium lt. W. T.

**Preparation and Reactions of Stannous Oxide and Stannous ydroxides.** FRANK WARD BURY and JAMES RIDDICK PARTING-ıN (T., 1922, **121**, 1998—2004).

**Reduction of Thorium Oxide by Metallic Tungsten.** THE ESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON 'ork conducted by COLIN JAMES SMITHELLS) (T., 1922, **121**, 36—2238).

**Germanium Hydride.** JOHN H. MÜLLER and NICOL H. ııTH (*J. Amer. Chem. Soc.*, 1922, **44**, 1909—1918).—Germanium ıy be detected by a modification of Marsh's test in quantities small as 0·00006 gram of the metal. The delicacy of the hydride ation is greatly increased by use of an alkaline generator as urce of nascent hydrogen. Aluminium and dilute potassium droxide solution serve best for the formation of large quantities germanium hydride, whilst sodium amalgam is best for small antities. A modification of the usual form of Marsh apparatus described which permits of the formation of a richer mixture of e hydride than has hitherto been prepared and still further reases the delicacy of the test. The apparatus is arranged follows:—an electrolytic hydrogen generator, using 15% sodium droxide as electrolyte and having nickel electrodes, a wash g tower containing a solution of a silver salt, a sulphuric acid ying tower, and a trap for exit of excess of hydrogen from e generator. The gas prepared and purified in the above train sses into the germanium hydride generator, which consists of small wash-bottle the inner tube of which is cut off at a height m. above the bottom of the bottle; the generator is fitted with funnel and stopcock through which the sodium amalgam and manium solution may be added after the whole system has been ed with electrolytic hydrogen. To the generator is attached a all drying tube and to the end of this a constricted tube in which e germanium mirror may be formed. A rich mixture of german-n hydride and hydrogen is obtained by placing dry sodium algam in the generator and expelling the air by means of electro-ic hydrogen. The hydrogen stream is then interrupted and an ueous solution of the germanium salt added and washed in with ter. The germanium hydride is then allowed to form in the

closed apparatus, and when the action is over swept through the heated constricted tube by means of electrolytic hydrogen, when a mirror of germanium is immediately formed. The decomposition *temperature of germanium hydride* lies between 340° and 360°, and the deposition of the mirror is best obtained below a red heat. The reverse action, involving the loss of germanium in hydrogen, has been quantitatively investigated and shows that at 750—800° 1·41855 grams of germanium loses 0·00647 gram when in a stream of hydrogen for thirty-eight hours. The dissimilarity of films of arsenic and germanium as obtained by the Marsh test is shown by a *spectroscopic examination of the light transmitted* by the films, and the thickness of the films has been determined. A study of the composition of the substance described by Voegelen (A., 1902, ii, 401) shows this substance to be a mixture which may contain little or much silver *germanide* $Ag_4Ge$ along with metallic silver, depending on the method used in the preparation of the hydride. The precipitate contains much more germanide if the hydride is generated by the action of potassium hydroxide on aluminium and passed slowly through a solution of a silver salt, whilst if the formation of the hydride is brought about by means of sodium amalgam or the gas passed rapidly through the silver salt, the precipitate contains little germanide and the solution contains germanic acid. Evidence is put forward which indicates the presence of at least one hydride other than the tetrahydride, but the presence of this hydride has not been finally established. The richest mixture of hydrogen and germanium hydride examined contained 0·176% of the hydride. J. F. S.

**Germanium Hydride.** FRITZ PANETH and EDGAR SCHMIDT-HEBBEL (*Ber.*, 1922, **55**, [*B*], 2615—2622).—Germanium hydride has been described previously by Voegelen, but its composition has not been settled definitely. The substance has now been re-examined, and since the authors had only a very limited amount of material at their disposal they have found it most convenient to prepare the gas by the action of zinc or, preferably, magnesium on a solution of germanium in the presence of 3—4*N*-sulphuric acid; the yield varies between 0·2 and 1·5%. The gas evolved from the solution is dried by passage over granulated calcium chloride and phosphoric oxide and subsequently led through a Landsiedl apparatus filled with potassium hydroxide solution (50%), a **U**-tube immersed in pentane cooled to −110° and finally through three **U**-tubes cooled in liquid air. The almost invisible white condensate in the last three tubes is analysed by the method used previously for antimony and tin hydrides (this vol., ii, 383). It is thus shown that the atomic ratio of hydrogen to germanium is exactly 4 : 1. The accuracy of the analyses excludes the possibility of the presence of more than the merest traces of possible hydrides, such as $Ge_2H_6$, and the existence of these is the more improbable, since, under the conditions of the condensation, they must have become concentrated in the condensate; the pentane tube does not retain any germanium compounds, and about 15%

of germanium hydride passes uncondensed through the apparatus. It is shown that the molecular formula of germanium hydride is $GeH_4$.

Germanium hydride is unusually stable, being unaffected by potassium hydroxide solution (50%) or phosphoric oxide, and requiring a relatively very high temperature to cause its certain decomposition. The colours of the germanium mirrors are extraordinarily varied and in this respect the metal is differentiated from all others which yield hydrides decomposable by heat. In doubtful cases, confirmation may be obtained by oxidising the mirror to colourless germanium dioxide by heating it in a current of oxygen and subsequently reducing it in hydrogen to copper-coloured germanium, which can then be dissolved in sodium hypochlorite. Arsenic exhibits greater solubility in the reagent, but its oxide would be volatilised completely under the experimental conditions. H. W.

**The System $Bi_2O_3$-PbO.** L. BELLADEN (*Gazzetta*, 1922, **52**, ii, 160—164).—The occurrence in nature of a series of minerals constituted of double sulphides of bismuth and lead which may mostly be regarded as derivatives of hypothetical ortho-, meta-, and pyro-sulphobismuthous acids renders possible the existence of similar compounds containing oxygen in place of the sulphur atoms. The author has investigated the fusion diagram of the system $Bi_2O_3$ : PbO, the results obtained indicating the formation of the compounds: (1) $4Bi_2O_3$,PbO, m. p. 695° (decomp.); (2) $3Bi_2O_3$,2PbO, m. p. 686°, stable when fused; (3) $Bi_2O_3$,2PbO, m. p. 625°, stable on fusion. These indications are fully confirmed by micrographic examination.

Litharge has m. p. 870° and bismuth trioxide, m. p. 817°.

T. H. P.

**Polonium Hydride. II.** FRITZ PANETH and ADOLF JOHANNSEN (*Ber.*, 1922, **55**, [*B*], 2622—2637).—Polonium hydride closely resembles bismuth hydride in the order of magnitude of its yields by all methods of preparation, its great instability during the condensation of minimal amounts, and its ready decomposability by chemical reagents.

The preparation of polonium hydride has been affected previously by the action of dilute acids on an electrolytic deposit of polonium on magnesium (A., 1919, ii, 76). Since it is difficult by this method to secure highly activated magnesium foil in uniformly good yield, a process has been evolved which depends on the deposition of polonium on magnesium powder by distillation. For this purpose, the polonium is first deposited electrolytically from a lead nitrate solution containing radium-*D* on the central portion of a thin piece of platinum foil. The latter is now suspended in a glass dish, the bottom and sides of which are covered with magnesium powder; the apparatus is brought into an evacuated desiccator and the foil is raised electrically to a bright yellow heat. The volatilised polonium is deposited mainly on the powder, which, after being carefully mixed, gives a preparation of uniform activity.

(A method for the recovery of polonium from its residual solution and again precipitating it on magnesium is described in detail. The yield of polonium hydride obtained by the solution of the activated powder in dilute acid is practically the same as from the activated foil, and lies intermediate between those of lead and bismuth hydrides. The formation of the hydride cannot be ascribed to the decomposition of a compound of magnesium and polonium since the gas is also obtained by adding magnesium powder to a solution containing polonium. The method of "spark electrolysis" is also applicable to the production of polonium hydride, but the evolution of the gas by this method is too irregular for use for the present purposes.

Polonium hydride which has been condensed at the temperature of liquid air is very extensively decomposed during re-evaporation. The action appears to depend to some extent on the accompanying gases; thus, for example, it has not been found possible to re-volatilise polonium hydride which has been prepared by "spark electrolysis." The condensation and partial re-volatilisation of polonium hydride affords the most conclusive evidence of the gaseous nature of the compound.

Phosphoric oxide causes very extensive decomposition of the hydrides of polonium and thorium-*C*, whereas calcium chloride has a less strongly marked action; the latter, however, can only be used for the desiccation of polonium hydride when a very high initial activity can be used. Under the experimental conditions adopted, unboiled distilled water only allows 3% of polonium hydride to pass unchanged, whereas 50% of the gas passes through air-free, distilled water. *N*/10-Sodium hydroxide and *N*/10-silver nitrate solution cause very extensive decomposition of polonium hydride.

The rates of spontaneous decomposition of polonium and bismuth hydrides have been examined; the former is decomposed to the extent of 50% after four minutes, the latter after about twenty-five minutes. A more exact calculation is not warranted by the accuracy of the experiments, which suffer under the disadvantage that the gases cannot be dried. It is, however, established that moist polonium hydride is considerably more easily decomposed than bismuth hydride. H. W.

**The Recrystallisation of Pure Mechanically Unworked Gold obtained by Solidification from the Fused Mass.** W. FRAENKEL (*Z. anorg. Chem.*, 1922, **122**, 295—298).—Pure mechanically unworked gold showed no change in size or form of crystals on heating at 1000—1040°. The purity could not be guaranteed to be such that the crystallites might not be surrounded by films of impurity (cf. Tammann, A., 1921, ii, 172). W. T.

## Mineralogical Chemistry.

**Colour of Fluorites.** TOKUTARO SAKAO and MITSUIE HIROSE (*Mem. Coll. Sci. Kyōtō*, 1921, **4**, 349—350).—The colour of fluorite crystals has been attributed by *Blount* and *Sequeira* (T., 1919, **15**, 705) to the presence of a small amount of organic matter. Employing the ultra-microscope, the authors were unable to detect the presence of such matter in a state of colloidal suspension in five varieties of coloured fluorite crystals. J. S. G. T.

## Analytical Chemistry.

**Qualitative Chemical Analysis.** V. MACRI (*Boll. Chim. Farm.*, 1922, **61**, 417—418).—By means of the following scheme, the use of sulphur compounds is avoided. The hydrochloric acid solution is placed, together with a rod of zinc, in a flask fitted with a gas delivery tube, the latter being heated so as to make a Marsh apparatus; the flask is eventually heated. The liquid is filtered, the precipitate containing silver, mercury, lead, bismuth, copper, cadmium, platinum, gold, tin, antimony, and arsenic. The filtrate is heated to boiling with zinc acetate, aluminium, iron, and chromium being precipitated. The filtrate from this is heated with hydrogen peroxide, which precipitates manganese. The filtrate from the latter is heated and treated with zinc oxide in presence of chlorine, nickel and cobalt being thus precipitated. Reference is made to various circumstances which prevent the subdivision into groups from being rigorously exact. [Cf. *J. Soc. Chem. Ind.*, 1922, 839A.] T. H. P.

**Quantitative Microanalysis.** MAURICE NICLOUX and GEORGES WELTER (*Chim. et Ind.*, 1922, **8**, 269—272).—A summary of Pregl's methods of microanalysis for use with which a Longue's aperiodic microbalance is recommended. A micro-method for the estimation of urea in blood is outlined (cf. this vol., ii, 170). W. G.

**Use of Resorcinol in Qualitative Inorganic Analysis.** LAVOYE (*J. Pharm. Belg.*, 1921, **3**, 889—890; from *Chem. Zentr.*, 1922, ii, 1154).—One c.c. of a 10% solution of resorcinol mixed with 2 c.c. of 10% ammonia solution gives characteristic colorations when added to 2 c.c. of different metallic salt solutions. The following colorations are obtained. Zinc salts, a yellowish-green colour, changing to deep blue; cadmium salts, a less intense blue colour; manganese salts, in the presence of ammonium salts, a bluish-green colour; nickel salts, bluish-green; copper salts, reddish-violet, changing to bluish-violet. With salts of the latter two metals the solutions should be so dilute that ammonia alone

gives no coloration. Platinum salts give a garnet-red colour; mercury salts give no colour, but the solution on evaporation gives crystalline needles. All the colorations mentioned change to red on the addition of acid. The reactions are sensitive with very small amounts of the metals in question. G. W. R.

**Analysis of Minerals by the Röntgen Spectrograph.** ASSAR HADDING (*Z. anorg. Chem.*, 1922, **122**, 195—200).—The suitability of this method is shown by the fact that monazite, which contains twelve oxides, only gives twelve lines. Quantities of substances are indicated roughly by the strength of the lines. Very small amounts of substances are shown by weak lines and the author suspects the presence of the unknown element of atomic number 61 in "fluocerite." W. T.

**Use of Mixed Indicators.** A. COHEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1851—1857).—It is shown that differences of subjective colour are enhanced when two indicators are partially transformed at the same hydrogen-ion concentration. The colorimetric determination of hydrogen-ion concentration can, therefore, be rendered more precise by the use of suitable mixed indicators and in certain titrations sharper end-points can be obtained, particularly in coloured liquids. Thus with the indicator bromothymol-blue the value $P_H$ 6·8 is indicated by a pure green colour, but in a yellow medium the colour is yellowish-green and difficult to observe; if, however, an indicator is added which is violet at this concentration, then the total effect of the mixed indicators will be a green end-point. This may be achieved by adding equal quantities of bromothymol-blue and bromocresol-purple. Several cases of the use of mixed indicators are described. J. F. S.

**Modification of the Chlorometric Method of Hayem and Winter.** J. MALGOYRE (*Bull. Soc. pharm. Bordeaux*, 1922, **60**, 59—64).—Gastric juice is treated with a reagent prepared by dissolving 2 grams of chromic acid in 100 c.c. of 95% ethyl alcohol to remove proteins, and then titrated directly. The free and total hydrochloric acid are estimated by the Topfer-Linossier method, and the combined acid found by difference. The total chlorine is estimated by neutralising 10 c.c. of gastric juice with a saturated solution of sodium carbonate, adding 10 c.c. of the chromic acid reagent, filtering, and titrating with 0·1*N*-silver nitrate. The fixed chlorine is equal to the difference between the total chlorine and total acidity. CHEMICAL ABSTRACTS.

**Reductions with Cadmium and Lead in Volumetric Analysis. III.** W. D. TREADWELL (*Helv. Chim. Acta*, 1922, **5**, 806—818).—[With P. HRISTIE, L. EGGER, and P. STURZENEGGER.] A warm solution of a chlorate in presence of sulphuric acid can be reduced quantitatively to chloride by passing it through a cadmium reduction tube (A., 1921, ii, 523), and the chloride can then be titrated by the Volhard process. Since perchlorates are not reduced under these conditions, chlorate can be determined in presence of perchlorate by this method. Perchlorate can be reduced to chloride

by boiling in sulphuric acid solution (about 10 c.c. of concentrated acid to 50 c.c. of $0{\cdot}1N$-chlorate solution) in presence of titanium sulphate for one-half to one hour with finely divided cadmium. The cadmium is only attacked to a slight extent by the acid, and a small amount of cadmium sulphide is formed which, however, does not interfere with the estimation of perchlorate. After cooling, the solution is diluted, the titanous sulphate present is carefully oxidised with permanganate and the chloride is titrated either by the Volhard process or electrometrically.

[With A. FREULER and A. WEBER.]—A reduction method for the estimation of columbium was described by Metzger and Taylor (A., 1909, ii, 702), depending on the stabilising effect of succinic acid on a solution of columbic acid in sulphuric acid. The solution was reduced with amalgamated zinc to the constant stage $Cb_2O_{3{\cdot}107}$. It has now been found that the succinic acid solution of columbic acid prepared in this manner is far from stable. In course of a few days it becomes opalescent and its reducibility gradually becomes less. The reducibility also becomes less when a solution of columbic acid in sulphuric acid is diluted, confirming the view that the reducibility depends on the dispersity of the colloidal acid. Consistent results were obtained when the reduction was carried out in a cadmium reduction tube in presence of ammonium molybdate or vanadate or of titanium sulphate, the subsequent titration being carried out with permanganate. The most stable solutions of columbic acid were obtained by dissolving the fluoride in concentrated hydrochloric acid, and consistent results were obtained when such solutions were reduced in a cadmium tube and titrated electrometrically with ferric chloride.

[With R. F. EDELMANN.]—A concentrated hydrochloric acid solution of a molybdate can be reduced quantitatively to the Mo''' stage by finely divided lead. Lead in a suitable form for a reduction tube was obtained by immersing a zinc rod in an acidified solution of lead acetate. The crystals of lead must be carefully washed with alcohol and ether, not pressed together. Stannic chloride was also reduced quantitatively to stannous chloride by means of lead. The oxidation titrations were carried out with permanganate. E. H. R.

**Chlorination of Mixed Silver Haloids in Gooch Crucibles.** M. G. MELLON and J. C. SIEGESMUND (*Proc. Indiana Acad. Sci.*, 1921, 197—199).—The crucible containing the silver haloids is placed inside a larger crucible which is covered with a watch glass with a hole in the centre. Chlorine is passed into the crucible through a tube extending to within 1 cm. of the bottom, the outer crucible being gently heated meanwhile.

CHEMICAL ABSTRACTS.

**Electrometric Titrations with Lead Nitrate.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 369—377).—Electrometric titration of iodide solutions, of not too low concentration, with lead nitrate solution yields trustworthy results, even in the presence of chlorides and bromides; the method is applicable to the estim-

ation of ferrocyanides and also of sulphates provided that mineral acids, ferric salts, and aluminium salts are not present. The titration of pyrophosphates with lead nitrate solution gives unsatisfactory results, but the method may be used in the case of a few organic salts such as oxalates, tartrates, and succinates.

W. P. S.

**A New Iodometric Method Based on the Formation and the Estimation of Cyanogen Iodide.** RUDOLF LANG (*Z. anorg. Chem.*, 1922, **122**, 332—348).—A volumetric method for the estimation of iodide is given, based on the fact that an iodide in hydrochloric or sulphuric acid solution is oxidised by an iodate or permanganate in the presence of hydrocyanic acid to cyanogen iodide, the end-point being indicated by starch solution. This can be controlled by estimating the cyanogen iodide with thiosulphate $ICN+2S_2O_3''+H^{\cdot}=I'+HCN+S_4O_6''$. The method is found to be applicable in the presence of bromides and nitrates. Different stages of oxidation of iodine can also be estimated in mixtures.

W. T.

**The Estimation of Sulphur in Vulcanised Rubber.** J. W. W. DYER and AMY R. WATSON (*J. Soc. Chem. Ind.*, 1922, **41**, 332T).—With reference to the method described for the estimation of combined sulphur in vulcanised rubber (this vol., ii, 656), the authors acknowledge priority of publication to A. R. Pearson (*Analyst*, 1920, **45**, 405). They prefer to use the method for combined sulphur only, however, and not for total sulphur, unless the amount of free sulphur is small.

G. F. M.

**Estimation of Sulphides by Oxidation with Ferric Salts.** P. P. BUDNIKOFF and K. E. KRAUSE (*Z. anorg. Chem.*, 1922, **122**, 171—174).—The estimation is based on the reaction $3Na_2S+3Fe_2(SO_4)_3=3Na_2SO_4+6FeSO_4+3S$. The amount of ferrous salt is found by permanganate. The acidity of ferrous sulphate is neutralised by the addition of alkali carbonate. The method is only applicable to sulphides which are soluble in water and acids.

W. T.

**The Estimation of Sulphuric Acid as Barium Sulphate in the Presence of Aluminium.** L. MOSER and P. KOHN (*Z. anorg. Chem.*, 1922, **122**, 299—310).—The results of the estimation of sulphuric acid in the presence of aluminium are too low, these low results being due to the presence of aluminium sulphate in the precipitate. The amount of this impurity increases up to a maximum with an increase in the concentration of the aluminium salt. Precipitated barium sulphate takes up aluminium sulphate from solution—a solid solution is thus indicated. The best results are obtained by working in hydrochloric acid solution when the maximum error is −0·15%. The errors observed in the presence of the aluminium-ion are only one-tenth those obtained in the presence of the ferric-ion.

W. T.

**A New Accelerator for the Destruction of Organic Matter in the Kjeldahl Method for the Estimation of Nitrogen.** M. SBOROWSKY and I. SBOROWSKY (*Ann. Chim. Analyt.*, 1922, **4**, 266—267).—Mercurous iodide accelerates the destruction of organic matter in the digestion with sulphuric acid much more effectively than metallic mercury or other mercury salts. In two experiments carried out with 10 c.c. of sulphuric acid, with mercurous iodide 0·7 gram of sugar was destroyed in the time required for the destruction of only 0·1 gram with metallic mercury. A digestion was completed in fifty to sixty minutes which with metallic mercury required four to eight hours. H. C. R.

**Estimation of Total Nitrogen in Fertilisers containing Nitrites and of Nitrite Nitrogen in the Presence of Nitrates.** F. MACH and F. SINDLINGER (*Z. angew. Chem.*, 1922, **35**, 473—474).—To estimate the total nitrite and nitrate nitrogen, 25 c.c. of an aqueous solution of the sample (this quantity of solution should contain not more than 0·05 gram of nitrogen) are added gradually to a boiling mixture of 30 c.c. of saturated potassium permanganate solution and 5 c.c. of dilute sulphuric acid (1 : 2); a further quantity of 10 c.c. of the acid is then added, the mixture is cooled, treated with 10 grams of ferrum redactum, and again boiled for about ten minutes. The resulting ammonia is estimated by distillation in the usual way. The nitrate nitrogen is then estimated in another portion of 25 c.c. of the solution by boiling this quantity for ten minutes with 30 c.c. of $N/3$-sulphuric acid and 10 c.c. of methyl alcohol (the whole of the nitrous acid is thus expelled in the form of its methyl ester), neutralising the cooled mixture, and reducing the remaining nitrate with ferrum redactum in sulphuric acid solution. The nitrite nitrogen is found by subtracting the nitrate nitrogen from the total nitrogen. If ammonium salts are present, the ammonia nitrogen must be estimated separately and an allowance made for its quantity. W. P. S.

**Comparison of the Methods for the Estimation of Nitric Oxide.** ALFONS KLEMENC and CORNELIE BUNZL (*Z. anorg. Chem.*, 1922, **122**, 315—331).—Nitric oxide was prepared according to the method of Emich (A., 1892, ii, 939); this, however, contained 1% of impurity and was purified by fractionation, using liquid air. The estimation of the gas by passing it over heated copper was found to give accurate results. Estimations (1) with hydrogen in the Drehschmidt platinum capillary (Knorre and Arndt, A., 1899, ii, 806), (2) by the method of Baudisch and Klinger (*Ber.*, 1918, **45**, 3231), and (3) by absorption with ferrous sulphate were found to give untrustworthy results. Good results were obtained by absorbing the gas by acidified bromate or $N/5$-potassium permanganate and estimating the excess. The latter method can also be used in the presence of carbon dioxide and other gases. W. T.

**Detection of the Nitrous Anion.** P. FALCIOLA (*Gazzetta*, 1922, **52**, ii, 87—89).—Small proportions of nitrite may be detected: (1) By the transitory yellow coloration obtained by acidification

with sulphuric acid and gradual addition of sodium thiosulphate solution. (2) By the orange colour developed on addition, to a litre of the solution, of about 2 c.c. of sulphuric acid, excess of thiocyanate, and about 0·1 gram of ferrous sulphate (cf. Horst, A., *1921*, ii, 461). (3) By the yellow coloration formed on addition of excess of aniline phosphate. [Cf. *J. Soc. Chem. Ind.*, 1922, 856A.]

T. H. P.

**Separation of Phosphoric Acid in Qualitative Analysis.** N. TARUGI (*Boll. Chim. Farm.*, 1922, **61**, 545—552).—The author's investigation of Gattermann and Schindhelm's proposal to eliminate phosphoric acid by means of stannic chloride (A., 1917, ii, 41) shows that, even under the best conditions, 15·4% of the total phosphoric acid passes into the filtrate from the stannic precipitate, and that the latter contains part of the iron, chromium, calcium, barium, etc., present. Further, when the proportion of phosphoric acid in the solution to be examined is unknown, it is impossible to add the exact quantity of ammonium phosphate to give a definite ratio between phosphate and stannic chloride. T. H. P.

**Effect of Iron on the Iodine Titration of Arsenite.** F. L. MELVILL (*J. S. African Chem. Inst.*, 1922, **5**, 3—5).—The interference of ferric salts in the titration of arsenite solution by iodine solution may be prevented by the following procedure. The slightly acid arsenite solution, containing not more than 0·1% of iron (expressed as $Fe_2O_3$), is treated with *about one-half the quantity* of iodine solution required to oxidise all the arsenite, 10 c.c. of saturated sodium hydrogen carbonate solution are then added, and the titration is completed. In this way the whole of the iron is precipitated as ferric arsenate and no longer interferes with the titration. W. P. S.

**Estimation of Boric Acid.** WILHELM STRECKER and ERNST KANNAPPEL (*Z. anal. Chem.*, 1922, **61**, 378—397).—The substance containing boric acid or its salts is mixed with 40% phosphoric acid and methyl alcohol and the mixture is distilled in a current of air saturated with methyl alcohol (the air is passed previously through a flask containing methyl alcohol) until all the methyl borate has been collected in a receiver containing sodium hydroxide solution. The distillate is then heated to expel methyl alcohol, treated with a slight excess of hydrochloric acid, using methyl-orange as indicator, boiled to expel carbon dioxide, and neutralised with sodium hydroxide solution. After the addition of mannitol in the proportion of 1 gram for each 10 c.c. of solution, the mixture is titrated with $N/10$-barium hydroxide solution, using α-naphtholphthalein solution as indicator. W. P. S.

**Sulphonated Derivatives of the Naturally Occurring Sulphidic Hydrocarbons.** C. PÉPIN and G. REAUBOURG (*J. Pharm. Chim.*, 1922, [vii], **26**, 258—261).—As the therapeutic value of ichthyol is largely dependent on the amount of "sulphidic" sulphur it contains as distinguished from total sulphur which

comprises in addition sulphonic and sometimes sulphatic sulphur, it is desirable that more precise standards should be laid down to which commercial ichthyol preparations should conform. Ammonium or other sulphates should be almost completely absent, as indicated by the formation of nothing more than an opalescence on the addition of barium chloride to the filtrate after precipitation of an ichthyol solution by albumin and hydrochloric acid. Sulphidic sulphur can only be estimated by difference by Thal's method, which consists in an estimation of total sulphur, by Carius's method, for example, and subtracting from this the sulphur present as sulphate, if any, determined by weighing the above barium sulphate precipitate, and the sulphonic sulphur determined by an ammonia estimation, and calculating on the basis of one sulphonic group for each molecule of ammonia after making allowance for the ammonia combined as sulphate. As thus estimated, "sulphidic" sulphur should represent at least 15% of the weight of the dried ichthyol. The conservation of ethylenic linkings in the preparation of the ichthyol should be confirmed by the decolorisation of bromine water. G. F. M.

**Radioactive Indicators.** FRITZ PANETH (*Z. angew. Chem.*, 1922, **35**, 549—552).—Use has been made of radioactive isotopes of metals such as lead and bismuth for indicating the presence of minute and unweighable quantities of these elements or their compounds. Quantities of the radioactive isotopes of the order of a millionth of a milligram are easily detected by the electroscope. Once mixed with the inactive isotope, they cannot be separated by chemical means, so that the presence of the radioactive isotope indicates the presence of the inactive one also. Practical applications have been made in analytical chemistry in determining the solubility of very sparingly soluble substances and in the study of adsorption phenomena. In electrochemistry it has been established by this means that an interchange of the metallic portion of the molecule actually occurs on mixing solutions of two salts of the same metal and subsequently recovering them from solution, but that no such interchange occurs when one or both the substances are non-ionised. The actual deposition of an unweighable quantity of metal on the electrode before the minimum potential of electrolysis is reached has also been established. In colloid chemistry, the active surface of powders has been measured for the first time by the use of a radioactive indicator, and the distinction between crystalloid and colloid in the diffusion of the former through parchment membranes has been studied down to a dilution of $10^{-11}$ mol. per litre. In inorganic chemistry, the conditions for the preparation of bismuth and lead hydrides were studied by this means and the method was successfully applied to the measurement of the gas-tightness of rubber fabrics for gas-masks. The kinetic theory has received further experimental confirmation by the actual proof of the movement of the molecules in molten lead and measurements of the movement of lead ions in lead chloride even below its melting point. H. C. R.

**Estimation of Small Quantities of Calcium.** PATRIC PLAYFAIR LAIDLAW and WILFRED WALTER PAYNE (*Biochem. J* 1922, **16**, 494—498).—The method described is suitable for estim ating calcium in amounts of the order of 0·1 mg., and gives result accurate to about 0·002 mg. The calcium is first precipitated a oxalate (in the case of blood serum, this may be done directl from the serum without previous ashing). After separation, th precipitate is dissolved in hydrochloric acid and the calcium repre cipitated in the form of calcium alizarinate by the addition c excess of alizarin in alcoholic solution, and, after warming, of few drops of strong ammonia. When crystalline, the precipitat is collected in a Gooch crucible, washed with dilute ammonia, an decomposed with a solution of oxalic acid in 50% alcohol. Th liberated alizarin is dissolved in 95% alcohol, made just alkalin with ammonia, and estimated colorimetrically by compariso with a standard solution of ammonium alizarinate. E. S.

**The Separation of Zinc from Other Metals, especiall Nickel.** ALOIS LUDWIG (*Z. anorg. Chem.*, 1922, **122**, 239–261).—Zinc can be separated from nickel by precipitation wit hydrogen sulphide in the presence of ammonium tartrate. Th latter salt forms stable complex compounds with nickel, whic may perhaps explain its action; the latter might, however, be due t the replacement of the freed mineral acid by the weaker tartari acid. Results are also given of attempts to effect the separatio by precipitation of zinc from zinc ammonium phosphate in neutra solution in the presence of neutral tartrates and thiocyanate These investigations are being continued. W. T.

**The Influence of the Alkalis on the Titration of som Metals with Ferrocyanide.** W. D. TREADWELL and D. CHERVE (*Helv. Chim. Acta*, 1922, **5**, 633—639).—The electrometric titratio of zinc with potassium ferrocyanide was described by Treadwe and Weiss (A., 1920, ii, 120). The sharpness of the end-poin depends on the insolubility of the ferrocyanide of the heavy meta but it is also dependent on the alkali metal used, since the pre cipitate is generally a double salt. When cadmium sulphate i titrated with potassium ferrocyanide in neutral or weakly aci solution, the end-point is indicated by a moderately sudden dro in potential, but only in a highly dilute solution has the precipitat the exact composition $CdK_2Fe(CN)_6$. In the presence of a rubidiur salt or a cæsium salt, however, the end-point is much sharpe probably because the alkali metals with higher atomic volume form less soluble double salts with cadmium ferrocyanide. Whe sodium ferrocyanide is used for the titration, the precipitate i the simple salt, $Cd_2Fe(CN)_6$. When a zinc salt is titrated wit potassium ferrocyanide the precipitate is $Zn_3K_2[Fe(CN)_6]_2$, bu with sodium ferrocyanide, $Zn_2Fe(CN)_6$, is obtained. In presenc of a potassium salt, however, sodium ferrocyanide gives the abov zinc–potassium salt, whilst in presence of a cæsium salt, potassiur ferrocyanide gives $ZnCs_2Fe(CN)_6$ with a very sharp end-poin Lead nitrate can be titrated with ferrocyanide in neutral solutio

ut lead ferrocyanide is very sensitive to acid; consequently zinc an be titrated with ferrocyanide in hot acid solution in presence f lead. The precipitate obtained from lead nitrate and potassium errocyanide is $Pb_2Fe(CN)_6$, but in presence of a cæsium salt the recipitate has the composition $Pb_3X_2[Fe(CN)_6]_2$, where X is robably entirely cæsium. The ferrocyanides of the bivalent eavy metals appear to be less soluble the smaller the atomic olume of the heavy metal. E. H. R.

**Estimation of Lead in Lead Amalgam.** M. G. Mellon nd H. F. Reinhard (*Proc. Indiana Acad. Sci.*, 1921, 189—195).—Existing methods are considered to be unsatisfactory for the stimation of small quantities of lead in the presence of large uantities of mercury. A weighed quantity of the amalgam is overed with 25 c.c. of a 10% solution of cupric nitrate and allowed o remain for fifteen to twenty-four hours; lead enters into solution, ut mercury does not. After decantation through a filter, the malgam is washed, and the filtrate treated with a few drops of cetic acid and sufficient potassium dichromate solution to precipitate the lead as lead chromate, which is washed in a Gooch rucible, dried at 120°, and weighed. Chemical Abstracts.

**The Kastle-Meyer Reagent as a very Sensitive Reagent or Copper.** Ottorino Carletti (*Boll. Chim. farm.*, 1922, **61**, 49).—A claim for priority (A., 1914, ii, 74) over Thomas and Carpentier (this vol., ii, 86). T. H. P.

**New Method for the Estimation of Manganese.** St. Minovici and Const. Kollo (*Chim. et Ind.*, 1922, **8**, 499—500).—Manganese may be estimated with accuracy, even when present n only small quantities, by precipitation as iodate by means of odic acid according to the equation $MnSO_4+2HIO_3=Mn(IO_3)_2+H_2SO_4$. A solution of about twice the theoretical quantity of odic acid is added to the manganese solution, and after warming or ten minutes on a water-bath twice the volume of alcohol is dded. After keeping for a short time, the precipitate is collected n a filter or Gooch crucible and washed with 70% alcohol saturated ith manganous iodate. The mother-liquor contains no traces of anganese, the iodate being insoluble in 70% alcohol in presence f iodic acid. In water at the ordinary temperature, its solubility 0·195%, and in 70% alcohol 0·005%. The precipitate of manganous iodate is finally dried at 100°, and weighed. The absolute ercentage error in the examples given varies from 0·16 to 0·63% hen quantities of the order of 0·1—0·3 gram of the hydrated ulphate are taken for estimation. G. F. M.

**A New Microchemical Method for the Identification of Tungsten.** J. A. M. van Liempt (*Z. anorg. Chem.*, 1922, **122**, 36—238).—A small quantity of sodium nitrite is melted on a latinum spoon and a little tungsten is thrown in; sodium tungstate formed. This is dissolved in a little water and tungstic acid recipitated by the addition of hydrochloric acid (1 : 1). This is ollected and then mixed with a few drops of concentrated

ammonia and placed on a slide. Ammonium paratungstate soon crystallises in four-cornered plates on the edges of the drop and as long needles in the centre. W. T.

**Glacial Acetic Acid Method for Estimating Uranium in Carnotite.** WILFRED W. SCOTT (*J. Ind. Eng. Chem.*, 1922, **14**, 531—532).—Half a gram of the ore is heated with 40 c.c. of dilute (1 : 1) nitric acid, the mixture is evaporated to dryness, the residue ignited, and then boiled for five minutes with a mixture of glacial acetic acid and nitric acid (100 : 5); the insoluble portion is separated by filtration and the filtrate is evaporated to dryness. This residue is ignited until it turns black and the extraction with the acetic acid–nitric acid mixture repeated; the filtrate obtained is evaporated, the residue dissolved in 10 c.c. of nitric acid and 40 c.c. of water, the solution neutralised partly with ammonia and ammonium carbonate is added in quantity sufficient to dissolve the precipitate of uranium carbonate which first forms. After the addition of an excess of 3 grams of ammonium carbonate and 5 c.c. of ammonia, the mixture is filtered, the filtrate is acidified with nitric acid, and heated to expel carbon dioxide. An excess of ammonia is then added and the boiling is continued until all the uraninm has been precipitated, which is denoted by the yellow solution becoming colourless. The precipitate is collected, washed with 2% ammonium nitrate solution, ignited, and weighed as $U_3O_8$. W. P. S.

**Reductions with Cadmium in Volumetric Analysis. II.** W. D. TREADWELL (*Helv. Chim. Acta*, 1922, **5**, 732—743).—[With M. BLUMENTHAL.]—Uranyl salts can be titrated by first reducing to the uranous stage and titrating back with potassium permanganate (cf. A., 1921, ii, 523). When zinc is used for the reduction, the reaction tends to go beyond the uranous stage to the U''' stage and the same occurs, although to a less extent, when cadmium is used. Owing to the ease with which tervalent uranium is oxidised by air to the uranous stage, any over-reduction can be corrected by allowing the reduced solution to run from the reduction tube drop by drop into a vessel open to the air. Oxidation from the uranous to the uranyl stage by means of air depends on the degree of acidity of the solution. To prevent such oxidation, the reduction is carried out in a 3·0*N*-sulphuric acid solution. When the electrometric method of titration is used over-reduction can be ignored, as the titre is given by the distance between the two breaks in the potential curve. Titanium and uranium may be estimated together by reducing in very dilute solution and titrating electrometrically with permanganate in an atmosphere of carbon dioxide, the two breaks in the curve representing the completion of oxidation of titanous and uranous ions respectively.

[With M. STÄRKLE.]—The accuracy of the electrometric method for titrating titanium after reduction with cadmium (*loc. cit.*) was confirmed by comparison with a gravimetric method. It is shown that small quantities of titanium can be estimated accurately by this method in presence of large quantities of iron, using potassium dichromate for the titration.

[With M. HOOFT.]—Careful experiments in which every precaution was taken to exclude air during the reduction and titration with permanganate show that vanadic acid is reduced quantitatively to the V'' stage by cadmium.

[With M. DREIFUSS and A. BOSSI.]—Indigotinsulphonic acid is reduced by finely divided cadmium in 0·2 to 0·5*N*-sulphuric acid solution to the leuco-stage, and can then be accurately titrated by means of ferric chloride by the electrometric method in an atmosphere of carbon dioxide. The course of the potential curve indicates that the oxidation proceeds in two stages, probably through a quinhydrone stage. Thioindigotin and methylene-blue can be estimated in the same way. [Cf. *J. Soc. Chem. Ind.*, 1922, Nov.] E. H. R.

**A Micro-method for the Estimation of Ethyl Alcohol in Blood.** ERIK M. P. WIDMARK (*Biochem. Z.*, 1922, **131**, 473—484).—A method is described suitable for estimating the alcohol in a drop of blood or in larger quantities. It depends on the absorptive power for alcohol of concentrated sulphuric acid containing a known amount of dichromate. The operations are conducted in a specially designed flask to avoid mixing and contamination of the standard dichromate by organic matter, and at a temperature of 50—60°. Absorption of the alcohol is complete within two hours. The excess of dichromate is estimated, after dilution with water, by potassium iodide and thiosulphate. Blank estimations are essential features. H. K.

**The Estimation of the Methyl Group in Methylated Thiolbenzenes.** J. POLLAK and ANNA SPITZER (*Monatsh.*, 1922, **43**, 113—120).—The estimation of the methylthiol group by a method analogous to Zeisel's process for estimating the methoxyl group is complicated by the fact that hydrogen sulphide and methylthiol are evolved along with methyl iodide during the decomposition by hydriodic acid. The process now described consists in decomposing the substance with hydriodic acid (*d* 1·7), and passing the volatile products through a paste of red phosphorus and weakly acidified cadmium sulphate solution, to remove hydrogen sulphide, and thence into alcoholic silver nitrate. The precipitate is ignited, and the mixture of silver and silver iodide completely converted into the iodide for weighing. C. K. I.

**Identification of Small Quantities of Terpineol Hydrate in Complex Mixtures.** G. DENIGÈS (*Bull. soc. pharm. Bordeaux*, 1922, **60**, 49—54).—The sample is moistened with a drop of ethyl alcohol on a glass slide, terpineol being deposited on the edge in tufts of prismatic needles; previous sublimation between two slides may be desirable. On addition of a drop of sulphuric acid, a yellow colour is produced, passing to orange on heating. Finally, on addition of a drop of a solution containing 0·5 gram of lævulose in 25 c.c. of ethyl alcohol and 75 c.c. of water, a carmine-red

**Estimation of the so-called Total Geraniol Content of Citronella Oil.** A. W. K. de Jong and A. Reclaire (*Perf. Essent. Oil Rec.*, 1922, **13**, 319—321).—Numerous samples of citronella oil were analysed by slightly varying methods in order to ascertain the reason for the different results often obtained by different operators. The maximum difference observed was 2·8%, the average difference 0·7%. The influence of acetic anhydride of higher percentage strength than usual (80%) was negligible, and sodium acetate dried over sulphuric acid did not give better results than the usual fused article. The method recommended is to heat 10 grams of the dry oil with 10 c.c. of 80% acetic anhydride and 2 grams of freshly fused sodium acetate for two hours. After cooling, 50 c.c. of water are added and the excess of anhydride is decomposed by warming and shaking. The acetylated oil is separated, washed with brine until neutral, and dried. About 1·5 grams are then saponified with $N/2$-alcoholic potassium hydroxide after neutralising any residual acidity. After two hours' boiling under reflux the excess of alkali is titrated back with $N/2$-sulphuric acid. G. F. M.

**Causse and Bonnan's Method for the Estimation of Dextrose.** R. Krull (*Pharm. Weekblad*, 1922, **59**, 1035—1039).—The unsatisfactory end-point referred to by Lemkes and Lansberg (this vol., ii, 724) is due to the fact that towards the end of the titration, when most of the cuprous oxide has been removed from the solution, dextrose is being added to a strongly alkaline solution, to which, as is well known, it is very sensitive. The abnormal course of Fehling's reaction with urine may be considered in the light of Benedict's reaction. The iodometric estimation is accurate to 0·1%. S. I. L.

**Apparatus for Facilitating the Estimation of Dextrose by Titration with Permanganate by the Mohr-Bertrand Method.** J. van der Haar (*Arch. Suikerind*, 1922, **30**, 213—216).—Precipitation is carried out in a 500 c.c. round flask, and the supernatant liquid siphoned slowly through a Soxhlet tube into an 800 c.c. bottle, the neck of which is of the same size as that of the round flask. The precipitate is washed with hot water and the washings are siphoned off. The Soxhlet tube is removed from the bottle and placed on the flask. A little ferrous ammonium sulphate solution is next run through the siphon into the Soxhlet tube and the remainder poured directly into the tube itself; the tube is rinsed, and the contents of the flask are titrated with permanganate after acidification with sulphuric acid.

Chemical Abstracts.

**Estimation of Sucrose in Presence of Other Sugars by means of Alkaline-earth Hydroxides.** A. Behre and A. Thöring (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 65—70).—Materi[al] containing about 20 grams of sucrose is heated with 1·2 grams o[f] ...v burnt lime in about 50 c.c. of water for one hour at 60—80°

Other sugars are destroyed, and the sucrose can be determined polarimetrically. A. G. P.

**Flax and Kindred Fibres. I. Behaviour and Structure of Textile Fibres, and a Convenient Method of Distinguishing Flax from Hemp.** C. R. NODDER (*Trans. Text. Inst.*, 1922, **13**, 161—171).—Flax and ramie fibres always twist in a clockwise direction when drying, whereas hemp and jute fibres twist in the reverse way, and cotton usually exhibits different twists in different parts of the same hair. An examination of about 100 fibres in a warm, dry room is sufficiently accurate for determining the proportion of flax and hemp in a mixture. The direction of twist is connected with the spiral, fibrillar structure of these "bast" fibres. This structure is best revealed by mounting the fibre in concentrated calcium chloride solution, tinged with iodine, and carefully compressing it by gentle pressure on the cover-slip. The fibre is easily made ten times its normal width and the spirals show as bright reddish-purple lines (the compressed parts) among brownish-yellow ones. The striations in the outer layer of flax and ramie cells form left-handed spirals, and those of hemp and jute right-handed spirals. It follows, therefore, that wetting of these fibres is accompanied by an untwisting of the fibrils which make up the outer layer of the cell-wall. The phenomena are discussed in the light of the physico-chemical properties of cellulose. J. C. W.

**Rapid Estimation of Acetic and Butyric Acids in Mixtures.** L. NOTENBAART (*Natuurwetenschapp. Tijdschr.*, 1921, **3**, 131—134).—After previous experimental determination of the distribution of acetic acid and butyric acid between water and toluene, the total quantity of acid present is estimated by titration with 0·04*N*-sodium hydroxide. After extraction of most of the butyric acid and a little of the acetic acid by shaking with an equal volume of toluene, the aqueous solution is again titrated.

CHEMICAL ABSTRACTS.

**Adaptation of the Pentabromoacetone Method to the Estimation of Citric Acid in Urine.** WILLIAM B. MCCLURE (*J. Biol. Chem.*, 1922, **53**, 357—363).—The pentabromoacetone method for the estimation of citric acid (cf. Kunz, A., 1915, ii, 595) cannot be applied directly to urine owing to the formation of other precipitates. Satisfactory results may, however, be obtained if the urine is first made alkaline with sodium hydroxide and then treated, in the cold, with animal charcoal, and if the pentabromoacetone is finally separated from small quantities of impurities by volatilisation. E. S.

**Estimation of Meconic Acid in Opium.** H. E. ANNETT and M. N. BOSE (*Analyst*, 1922, **47**, 387—391).—Five grams of opium are triturated with 50 c.c. of water and after keeping over-night 40—45 c.c. of the filtered liquid are treated with 6 c.c. of 50% calcium chloride solution and kept a further twenty-four hours,

The precipitate, which is almost white, consists of calcium meconate and sulphate. It is collected, washed until the washings are colourless, and dissolved in 15 c.c. of 1·25*N*-hydrochloric acid. After keeping for twenty-four hours, pure meconic acid will have separated in white, crystalline scales. It is collected, washed twice with 0·5 c.c. of water, dried over sulphuric acid, and weighed as $C_7H_4O_7,3H_2O$. To the weight found 0·0213 gram is added, to correct for the solubility of meconic acid in 15 c.c. of 1·25*N*-hydrochloric acid. The figure obtained is multiplied by the factor depending on the amount of the aliquot portion of the solution taken for analysis, and then by the factor 10/9, to correct for the amount of meconic acid unprecipitated by calcium chloride, in order to arrive at the weight of acid in 5 grams of opium. G. F. M.

**Pregl's Solution.** M. BACHSTEZ (*Ber. Deut. pharm. Ges.*, 1922, **32**, 216—221).—Discrepancies between the analyses of Pregl's solution made by different observers indicate that its composition is variable in spite of assurances to the contrary given by the makers. A solution prepared by dissolving 0·0165 gram of sodium iodate and 0·65 gram of potassium iodide in 100 c.c. of water with the addition of 10 drops of *N*/10-hydrochloric acid gave very similar results to Pregl's solution when tested quantitatively for total, active, and free iodine. Its physiological and bacteriological properties were also similar to those of Pregl's solution. E. H. R.

**The Sulphuric Acid Reaction for Liver Oil.** H. D. RICHMOND and E. H. ENGLAND (*Analyst*, 1922, **47**, 431).—Constant results were obtained in testing cod-liver oil by the dilution method (Drummond and Watson, this vol., ii, 665) by adding 1 c.c. of the cod-liver oil to 10 c.c. of liquid paraffin (B.P.), mixing, and transferring 10 drops of the mixture to a white porcelain basin, adding 1 drop of sulphuric acid (B.P.) and stirring with a glass rod. If a transient purple colour developed, liquid paraffin was added in successive quantities of 5 c.c. until no purple coloration was given, and the dilution at which a faint transient purple was seen was recorded. If no purple was seen, successive additions of 1 c.c., 1 c.c., 2 c.c., and 5 c.c. of cod-liver oil were made. H. C. R.

**Properties and Preparation of Dutch East Indies Sandal Wood Oil.** A. ROJDESTWENSKY (*Perf. Essent. Oil Rec.*, 1922, **13**, 331—332).—The amount of oil obtainable from Dutch Indian sandal wood varies from 3·8—5·8%, and has the following characters: $d^{15°}$ 0·9745—0·9842, $\alpha_D^{28}$ −16·4 to −18·4, santalol content ...·7—98%; $n_D^{28}$ 1·5000—1·5013, soluble in 3—4 vols. of 70% ...ol. The quantity of oil obtainable from a sample may ...ertained by *distilling not more than 0·5 kilo. of shavings* ...ater after soaking for forty-eight hours. After ten to ...urs, the colour of the oil begins to darken, and in twenty ... distillation is finished. The first and last runnings do ...eatly in properties. G. F. M.

**Importance of Dimethylhydroresorcinol for Detection of Volatile Aldehydes in Body Fluids. The Identification of Formaldehyde in Urine after Administration of Hexamethylenetetramine.** WILHELM STEPP (*Biochem. Z.*, 1922, **130**, 578—581).—After administration of hexamethylenetetramine to a patient with kidney disease, formaldehyde was recognised in quantity in the urine by combination with dimethylhydroresorcinol.
H. K.

**A Modified Schiff's Solution.** E. WERTHEIM (*J. Amer. Chem. Soc.*, 1922, **44**, 1834—1835).—Rosaniline hydrochloride (0·005 gram) is dissolved in hot water (50—100 c.c.); the solution is filtered if necessary, diluted to 300 c.c. and cooled with running water. Sodium hyposulphite (6 grams) is added to the cooled solution. The salt dissolves completely in a few minutes, after which the solution is ready for use. If it is boiled for one minute (not longer) it first becomes red and subsequently practically colourless. It may now be heated in testing for aldehydes in order to hasten the test. Used in this manner, the solution gives the aldehyde test in about half the time required for the ordinary Schiff's test, although without heating it is usually a little slower than the ordinary Schiff's solution. Special precautions in preserving the solution are unnecessary. H. W.

**Comparative Estimations of Acetone in Urine.** KURT KÄDING (*Biochem. Z.*, 1922, **130**, 448—458).—A comparison has been made of various methods, suitable for clinical purposes for the estimation of acetone in urine. Scharf's metbod (*Med. klin.*, 1921, **36**), like Schall's method, is a modification of Legal's test and is the most suitable. H. K.

**The Characterisation of the Colouring Matter of Saffron: Its Use in Investigations Relating to Laudanum Poisoning.** MARCEL GUERBET (*J. Pharm. Chim.*, 1922, **26**, 218—220).—The coloration produced by the action of concentrated sulphuric acid on crocetin may be used for the detection of the colouring matter of saffron which yields crocetin on hydrolysis. This test may be used in the case of poisoning by drugs which are coloured with saffron. H. J. E.

**A Qualitative Test for Tannin.** ETHEL ATKINSON and EDITH OLIVE HAZLETON (*Biochem. J.*, 1922, **16**, 516—517).—A piece of gold-beater's skin is pinned on a surface of paraffin wax, soaked in water, and then covered with an aqueous extract of the material to be tested. After about fifteen minutes it is washed, treated with a 1% solution of ferric chloride, and again washed. If the skin is stained, the presence of tannin is indicated. E. S.

**Estimation of Indican in Blood-serum.** J. SNAPPER and W. J. VAN BOMMEL VAN VLOTEN (*Klin. Woch.*, 1922, **1**, 718—721; from *Chem. Zentr.*, 1922, ii, 1122).—In the estimation of indican

ı serum, a stronger reaction is given after precipitation with :ichloroacetic acid than after precipitation with alcohol. The )llowing procedure is recommended. The serum is precipitated ith an equal volume of 20% trichloroacetic acid. 2·5 C.c. of the ltrate are diluted to 10 c.c. with water and after addition of 1 c.c. f thymol in alcohol (5%) and 10 c.c. of Obermayer's reagent, left )r twenty minutes. The liquid is then extracted with 2 c.c. of hloroform and the reading taken after thirty minutes. With weak positive reaction a slightly increased indicanæmia is ıdicated, implying hypofunction of the kidneys (niereninsuffizienz). n acute nephritis, *hyperindicanæmia* implies a more marked ıtoxication than does retention of urea alone. The principal recautions to be observed in the estimation are given.

G. W. R.

**Detection of Urea in Tissue by Means of Xanthydrol.** [. BONNET and J. HAUSHALTER (*Compt. rend. Soc. Biol.*, 1922, 6, 395—397; from *Chem. Zentr.*, 1922, ii, 922).—For the micro-hemical detection of urea, the fixation of the tissue in a 10% solution f xanthydrol in ethyl alcohol and pure acetic acid in the ratio : 7 is recommended. G. W. R.

**A Reaction of Urea with *p*-Dimethylaminobenzaldehyde.** [. K. BARRENSCHEEN and O. WELTMANN (*Biochem. Z.*, 1922, **31**, 591—595).—The yellowish-green coloration obtained in dilute rine on addition of Ehrlich's aldehyde reagent is due to urea. he reaction can be used for the recognition of residual nitrogen ı serum freed from proteins by trichloroacetic acid when it exceeds 3—40 mg. %. H. K.

**Accurate Ureometer.** ANTONIO SCIORTINO (*Arch. Farm. ›erim. Sci. aff.*, 1922, **33**, 186—189).—The modified apparatus ›r the estimation of carbamide described allows of the use of ırying quantities of the urine, blood, etc., and of arbitrary amounts ; the sodium hypobromite. Equilibrium may be established ›tween the external and internal pressures prior to the reaction ıd completion of the latter assured by shaking the reaction bottle ıder diminished pressure. The volume of the nitrogen formed read in a burette graduated to 0·05 c.c. T. H. P.

**The Estimation of Urea in Urine by the Hypobromite [ethod with Complete Yield.** (MLLE) M. JANET (*J. Pharm. him.*, 1922, **26**, 161—170).—Sodium hypobromite, under the ıual experimental conditions, gives results which indicate only )—92% of the actual urea present. The method described is ıid to be accurate within 1% when compared with results obtained y standard gravimetric methods. The solution containing urea diluted, if necessary, so that the concentration is not much above % and a considerable excess of sodium hydroxide is added followed y the hypobromite. The presence of creatinine introduces a ight error: this is stated to be negligible. If ammoniacal com-

pounds are present, the whole of their combined nitrogen is liberated by the action of sodium hypobromite and sodium hydroxide so that the nitrogen due to urea is found by difference after estimating the ammonia. H. J. E.

**Electrometric Titration of Ferrocyanides.** ERICH MÜLLER and HANS LAUTERBACH (*Z. anal. Chem.*, 1922, **61**, 398—403). —The end-point of the titration of ferrocyanides in sulphuric acid solution with permanganate solution may be determined accurately electrometrically in cases where the titration has to be made under artificial light; the results obtained agree with those found where the end-point is denoted by the pink coloration of the slight excess of added permanganate. W. P. S.

**A Test for Pyridine.** FRIEDRICH LEHNER (*Chem. Z.*, 1922, **46**, 877).—If a few drops of aniline are added to a solution of pyridine containing water and a trace of cyanogen bromide, a red colour is immediately obtained and crystals of 2-anilinodihydropyridine phenyl bromide separate. One part of pyridine in 350,000 parts can be detected in this way. H. C. R.

**Detection of Small Quantities of Pyridine.** A. GORIS and A. LARSONNEAU (*Bull. Sci. Pharmacol.*, 1921, **28**, 497—498; from *Chem. Zentr.*, 1922, ii, 731).—By addition of aniline to a solution of pyridine in the presence of cyanogen bromide, 1-*anilinodihydropyridinium phenyl bromide*, a red substance, is formed. The coloration is noticeable even with one drop of pyridine in 10,000 c.c. of water. This reaction takes place even in the presence of pyrrole derivatives. G. W. R.

**A Reaction of Veronal and of the Hypnotics Derived from Barbituric Acid.** RENÉ FABRE (*J. Pharm. Chim.*, 1922, [vii], **26**, 241—249).—Veronal and other hypnotics of the barbituric acid series are readily condensed with xanthydrol to form crystalline dixanthyl derivatives by heating at 100° for about one minute an approximately 10% solution of the hypnotic in acetic acid with twice its weight of xanthydrol. After keeping for a few hours, the product is separated and washed with a little boiling alcohol, and is then sufficiently pure for melting-point determination. The m. p. of the principal dixanthylbarbituric acids are as follows: dixanthylveronal 245—246°, dixanthylphenylethylbarbituric acid 218—219°, and dixanthyldiallylbarbituric acid 242—243°. Similar derivatives are not formed by other hypnotics, and the reaction is therefore valuable for the characterisation and identification of the barbituric acids for both pharmaceutical and toxicological purposes, as it can easily be carried out with as little as 0·01 gram of the substance, or with the crude product obtained by the usual methods in toxicological investigations from the viscera, etc. G. F. M.

**The Estimation of Uric Acid.** HENRY JACKSON, jun., and WALTER W. PALMER (*J. Biol. Chem.*, 1922, **53**, 373).—A simplified

method for the preparation of the modified phosphotungstic acid reagent (this vol., ii, 328) is described. E. S.

**Estimation of Uric Acid in Blood.** L. BAUMAN and L. M. KEELER (*J. Lab. Clin. Med.*, 1922, **7**, 551—552).—A modification of Folin and Wu's method in which calibrated Lovibond tintometer glasses replace standard uric acid solution. A red glass (0·4) is placed over the unknown solution and a blue glass (2·9) over the opposite prism in a Duboscq colorimeter; the blue compound is developed without the use of sodium sulphite. The glasses may also be used with the Bock-Benedict colorimeter if the red glass is placed over the immersion cylinder and the blue in front of and parallel to the standard cell. The method is of general application; the use of glasses shortens the time of procedure and removes uncertainty arising from the possible decomposition of the standard uric acid solution. Precipitation may be avoided by addition of three drops of a solution of gum acacia preserved with thymol.

CHEMICAL ABSTRACTS.

**Estimation of Uric Acid and Urates in Blood.** CH. O. GUILLAUMIN (*Compt. rend. Soc. biol.*, 1922, **86**, 194—196; from *Chem. Zentr.*, 1922, iv, 111; cf. this vol., ii, 170—171).—Blood is freed from albuminous substances and a volume of the filtrate corresponding with 2 c.c. of plasma, clot, or total blood is treated with 1—2 c.c. of 0·9—1·0% sodium chloride solution and sufficient 40% sodium carbonate solution to give an alkaline reaction to litmus. Five c.c. of Folin's silver reagent are added, and, after mixing, the liquid is centrifuged. The clear liquid is removed and the precipitate treated with 2 c.c. of a solution of sodium chloride containing hydrochloric acid and 7—8 c.c. of water, and again centrifuged. The clear liquid obtained is treated with 0·5 c.c. of a solution of 2·5 grams of sodium cyanide and 5 grams of sodium sulphite in 100 c.c. of water, 1·5 c.c. of sodium carbonate solution, made up to 12·5 c.c., and, after addition of Folin and Denis's phosphotungstic acid reagent, compared with a standard uric acid solution. G. W. R.

**Estimation and Constitution of a Fraction of the Uric Acid in Blood.** CH. O. GUILLAUMIN (*Compt. rend. Soc. biol.*, 1922, **86**, 258—260; from *Chem. Zentr.*, 1922, iv, 111; cf. preceding abstract).—Direct estimation of uric acid in serum freed from albuminous substances gives higher results than those obtained by the Folin and Denis phosphotungstate method. The difference corresponds with a portion of the uric acid of the blood which is associated with fractions of the original nuclein complex. For its estimation (by difference) the preliminary removal of albuminous substances is preferably effected by using metaphosphoric acid.

G. W. R.

**The Volatilisation and Hydrolysis of Atropine in Toxicology.** PAUL HARDY (*J. Pharm. Chim.*, 1922, **26**, 220—226).—The author has investigated the error in estimations of atropine

due to losses by reason of volatility and hydrolysis, and finds that no loss occurs in extraction of the alkaloid, as it is not volatile in alcohol, ether, or chloroform vapour. In the case of water, atropine was detected in the distillate on boiling. Hydrolysis occurs readily in aqueous solution, increasing considerably with temperature; it is more rapid in alkaline than in neutral solution, but ammonia is not such an active hydrolytic agent as sodium hydroxide. H. J. E.

**The Estimation of Creatinine.** K. PFIZENMAIER and S. GALANOS (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 29—41).—The method given in the *Schweizerisches Lebensmittelbuch* (3rd ed., p. 72) for the estimation of creatinine is rapid and simple, but can be successfully used only when light-coloured solutions are available for colorimetric comparison and a colorimeter of the Duboscq type is used. If the solutions are dark in colour or contain sugar, the method fails, as animal charcoal cannot be used because it adsorbs creatinine. The colorimetric comparison in cylinders as specified in the book was found to be unsatisfactory. The method of Sudendorf and Lahrmann (*Z. Unters. Nahr. Genussm.*, 1915, **29**, 1) can always be used and is the only one available for use with dark-coloured solutions. If the authors' instructions are exactly followed and too great an excess of potassium permanganate —especially with very dark-coloured solutions—is avoided, accurate results are always obtained. The methods referred to are given in detail. H. C. R.

**An Apparatus for the Extraction of Theobromine and Caffeine by means of boiling Chloroform.** O. P. A. H. SCHAAP (*Pharm. Weekblad*, 1922, **59**, 920—923).—The Soxhlet extractor is modified to allow of heating by means of a water-bath. Exact dimensions and procedure are laid down (cf. *J. Soc. Chem. Ind.*, 1922, 781A). S. I. L.

**Estimation of Yohimbine in Yohimba Bark.** ARNOLD SCHOMER (*Pharm. Zentr.-h.*, 1922, **63**, 385—386).—In applying a method described previously (A., 1921, ii, 360) to barks containing but little yohimbine, the results obtained are more trustworthy when the crystallisation of the yohimbine hydrochloride is made in the cold. The impure hydrochloride, after treatment with 5 c.c. of ether and evaporation of this solvent, is dissolved in 3 c.c. of absolute alcohol and the solution is kept at 0° for eighteen hours. The crystals which form are collected, washed with a small quantity of chloroform, then with ether, dried at 100°, and weighed. W. P. S.

**Identification of Traces of True Albumin in Urine. Separation of *pseudo*Albumins.** M. RENOUX (*J. pharm. Belg.*, 1922, **4**, 381—382).—As a result of tests with a solution of egg-albumin, the author concludes that either neutral crystals of sodium sulphate or magnesium sulphate may be used for the defecation of urine

(after being made alkaline), preparatory to testing for traces of true albumin. CHEMICAL ABSTRACTS.

**The Estimation of Total Albumin in the Spinal Fluid.** J. B. AYER and H. E. FOSTER (*Repert. pharm.*, 1922, **34**, 114—115).—The albumin is precipitated with thiosalicylic acid and compared with the precipitate obtained from blood serum of known albumin content. The method is very exact. The normal quantity of albumin in 100 c.c. of fluid varies between 16 and 40 mg. (average 25 mg.). It is usually increased in pathological conditions. The authors give the albumin content found in a number of cerebrospinal diseases. CHEMICAL ABSTRACTS.

**The Estimation of Albumose-Silver.** J. HERZOG (*Pharm. Z.*, 1922, 67, 802—803).—One gram of the silver-protein is dissolved in 10 c.c. of water and 10 c.c. of concentrated sulphuric acid added in a thin stream. Two grams of finely powdered potassium permanganate are added in small portions with vigorous shaking. After fifteen minutes, the solution is diluted with 50 c.c. of water and ferrous sulphate added in small portions to decolorise the solution. The silver is then titrated with $N/10$-ammonium thiocyanate solution, the oxidised iron acting as indicator. H. K.

**The Estimation of Fibrinogen. Protein Estimations in Salt Plasma. Question of the Utility of Serum for the Quantitative Investigation of Blood.** G. LEENDERTZ and B. GROMELSKI (*Arch. expt. Path. Pharm.*, 1922, **94**, 114—123).—Indirect methods for the estimation of fibrinogen in blood are based on the fact that the fibrinogen content is equal to the difference between plasma- and serum-proteins. Since, however, serum formed by the spontaneous coagulation of blood contains water and chlorides emanating from the corpuscles, this relation only holds when the serum is obtained from separated plasma. Applications of the refractometric method to the indirect estimation of fibrinogen have not hitherto been successful when oxalate plasma has been used. Such failures have been due to two causes—the formation of a precipitate and the production of hypertonic plasma by the addition of sodium oxalate to blood. By using a 3·55% solution of sodium citrate, which is isotonic with blood and does not produce a precipitate, as anti-coagulant, the refractometric method may be readily applied. Two such methods, based on the above considerations, are described. E. S.

**Estimation of Hæmoglobin.** E. MEULENGRACHT (*Fol. hæmatol. I. Archiv*, 1921, 27, 1—9; from *Chem. Zentr.*, 1922, ii, 849).—Observations on the working details of hæmoglobin timations by Sahli's and by Autenrieth's methods. It is held the former is superior to the latter for clinical work. G. W. R.

**The Colorimetric Estimation of Hæmoglobin with Especial Reference to the Production of Stable Standards.** EDWIN H. TERRILL (*J. Biol. Chem.*, 1922, **53**, 179—191).—Stock solutions of acid hæmatin such as those of Cohen and Smith (A., 1919, ii, 532) and Robscheit (A., 1920, ii, 339) suffer from the disadvantages that the colour both changes and fades on keeping, whilst a turbidity is produced on dilution. Two modified methods for the preparation of acid hæmatin standards are therefore described. The first results in the formation of a concentrated stock solution which may be diluted, especially when the diluting fluid contains glycerol, without the production of a turbidity; although it fades slowly, it does not change qualitatively in colour. The second gives an acid hæmatin protein powder which is quite stable in the dry state and forms clear solutions in water and in 0·1*N*-hydrochloric acid. After standardisation, weighed quantities may be used for the preparation of standard solutions. A method is also described for the preparation from the powder of gelatin films of acid hæmatin which may be used with advantage in place of the glass plates of Newcomer (A., 1919, ii, 179).

In estimating hæmoglobin, the laking of the blood with water prior to acidification is recommended. Direct acidification produces a turbidity which leads to high results when a clear standard is used. Heat should not be employed to develop maximum colour as this again produces a turbidity. E. S.

**Estimation of Bilirubin in Blood.** PAUL HOLZER and HEINZ MEHNER (*Klin. Woch.*, 1922, **1**, 66).—Meulengracht's (*J. Amer. Med. Assoc.*, 1920, **74**, 68) method is worthless for the estimation of small amounts of bilirubin, and untrustworthy for the estimation of large amounts. To obtain accurate results it is necessary to enhance the bilirubin colour by diazotisation; Bergh's ("Der Gallenfarbstoff im Blute," 1918) method is the most trustworthy, whilst that of Haselhorst (A., 1921, ii, 472) gives inaccurate results for small concentrations of bilirubin.

CHEMICAL ABSTRACTS.

**[Detection of Bile Pigments in] Gastric Juice.** FRANZ UTZ (*Süddeutsch. Apoth.-Ztg.*, 1922, **62**, 77—78; from *Chem. Zentr.*, 1922, ii, 921—922).—In examination of the contents of the stomach for bile pigments, the filtrate should not be used, as the pigments are retained by the filter. Directions are given for the use of the Gmelin and Plesch tests for bile pigments and for the detection of rennin. G. W. R.

**Modification of the Iodine Test for Bile Pigments in Urine.** ERNST SILBERSTERN (*Zentr. inn. Med.*, 1922, **43**, 185—187; from *Chem. Zentr.*, 1922, ii, 850).—The ordinary reaction is modified, whereby the urine under examination is shaken with a solution of 0·5 gram of iodine in 36 grams of ether or 76·5 grams of chloroform (1 c.c. of this solution to 2—4 c.c. of the liquid to be tested). The excess of iodine remains in its original solvent whilst the

biliverdin colours the aqueous phase. In neutral solution, the reaction is more sensitive than the Gmelin test, although less sensitive in alkaline solution. The chloroform solution is preferable to the ethereal solution. G. W. R.

**Tests for Liver Function.** LEPEHNE (*Münch. Med. Woch.*, 1922, **69**, 342—344; from *Chem. Zentr.*, 1922, ii, 921).—Hay's flowers of sulphur test for bile acids in duodenal juice and urine is described in application to certain pathological conditions.
G. W. R.

**Estimation of the Activity of Invertase.** T. SWANN HARDING (*Sugar*, 1922, **24**, 89—90; from *Chem. Zentr.*, 1922, ii, 1032).—A solution of sucrose, approximately 10%, is prepared so that on addition of 5 c.c. of water to 50 c.c. of the solution a reading of $+33{\cdot}5°$ $V\pm1°$ is given in Schmidt and Haensch's polarimeter. The reading being accurately determined after acidifying with acetic acid, 5 c.c. of invertase solution are added and, after keeping at 30° for ten minutes, the solution is rendered alkaline by addition of sodium carbonate solution. The change in polarimeter reading is taken as a measure of the activity of the invertase solution. Ordinary invertase solutions change the polarimeter reading from $+33{\cdot}5°$ $V$ to $+23-10°$ $V$, the most active invertases giving 10° $V$. Invertases which diminish the reading to $+18$—$20°$ $V$ invert a 10% sucrose solution within half an hour. G. W. R.

**Analysis of Blood.** F. UTZ (*Pharm. Zentr.-h.*, 1922, **63**, 425—430).—A procedure is given for a complete examination of blood, and the methods used are described in detail. The following estimations should be made, the figures in brackets being the values obtained for normal blood: *Blood*, sp. gr. (1·050 to 1·060) and *total solids* (21 to 22%). *Blood-serum*, sp. gr. (1·027 to 1·032), refractive index ($n_D$ 1·343 to 1·350), freezing point (−56°), total solids (6 to 10%), total nitrogen (1·04 to 1·2%). *Blood-serum after removal of proteins by uranium acetate*, nitrogen (0·02 to 0·035%), urea (0·02 to 0·04%), uric acid (0·0025 to 0·0035%), creatinine (0·001%), reducing sugars (0·06 to 0·12%), sodium chloride (0·56 to 0·60%), and indican (0·045 mg. per 100 c.c.).
W. P. S.

## General and Physical Chemistry.

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**The Refractive Indices of Phosphorescent Sulphides.** Maurice Curie (*Compt. rend.*, 1922, **175**, 617—619).—Direct determination of the refractive indices of phosphorescent sulphides gives, for yellow light, values between 2·10 and 2·15. An appreciable fraction of each substance gives figures ranging to a lower limit of 1·6, whilst for no portion did the refractive index exceed 2·20. According to the work of Lenard (A., 1910, ii, 369) and Schmidt (*Ann. Physik*, 1922) the values should lie between 2·70 and 3·16, so that Lenard's interpretation of the constancy of the ratio $\lambda/\sqrt{K}$ does not appear to be well founded. H. J. E.

**Quantum Theory of Line Spectra.** N. Bohr (*Danske Vid. Selsk. Skrifter, nat. mat. Afd.*, 1918, **4**, [8], 1—100; from *Chem. Zentr.*, 1922, iii, 221—223).—Theoretical. The author develops his quantum theory of line spectra with special reference to the hydrogen spectrum, and to the Stark and Zeeman effects.
G. W. R.

**The Intensities of the Lines in the Balmer Series of Hydrogen.** Masamichi Kimura and Mitsuhara Fukuda (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 165—168).—The intensity distribution of the hydrogen lines in the Balmer series is greatly affected by the pressure of hydrogen. The addition of the vapours of hydriodic acid, iodine, sulphur, mercury, or sodium exerts an effect similar to that obtained on increased pressure. These gases suppress the higher members of the Balmer series and appear to exert a specific effect on the hydrogen atoms. The results on the action of iodine vapour are in disagreement with those of Holtzmark (A., 1918, ii, 283). W. E. G.

**The Broadening of the Balmer Lines of Hydrogen with Pressure.** E. O. Hulbert (*Astrophys. J.*, 1922, **55**, 399—405).—Experimental evidence is adduced for abandoning, as a cause which interferes with the absolute homogeneity of spectrum lines, the consideration of disturbance depending on collision with other particles, and suggesting that the principal cause of the widening of the lines is the influence of an electric field on the radiating particle (cf. Merton, *Proc. Roy. Soc.*, 1915, **92**, 322).
A. A. E.

**Influence of Gases and Vapours on the Intensities of the Lines of the Secondary Spectrum of Hydrogen.** Masamichi Kimura and Mitsuhara Fukuda (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 153—163).—The intensities of the lines in the hydrogen secondary spectrum are modified by pressure, and the addition of gases and vapours. Increase in pressure weakens those lines in the secondary spectrum on the long wave-length side of λ 6240, and in the region

between λ 5690 and $H_\beta$. Between these two regions, the lines undergo selective changes in intensity. The Fulcher group I lines are relatively intense at low pressures, whilst those belonging to group II are weak. The addition of helium, mercury, or bromine to the spectrum tube produces similar changes in the intensities of the lines to those obtained on increase of pressure, although helium exerts a specific effect on some of the hydrogen lines. The suggestion is made that the hydrogen molecule can be reformed either by the combination of a positively charged molecule and an electron, or by the association of two neutral atoms, and that the two groups of lines owe their existence to the occurrence of these two distinct processes. W. E. G.

**The Continuous Spectrum of Hydrogen in the Schumann Region.** E. P. LEWIS (*Physical Rev.*, 1920, **16**, 367—368; cf. *Science*, 1915, **41**, 947).—By the use of a fluorite vacuum spectrograph it has been found that the continuous spectrum of hydrogen extends with undiminished intensity well into the Schumann region. At λ 1800 it begins rather suddenly to diminish in intensity, and disappears at about λ 1750. Slightly below λ 1700, the line spectrum of hydrogen reappears, with no trace of a continuous background. Attention is directed to the fact that the continuous spectrum completely fills the region between the Balmer series and the Schumann line spectrum, with no lines whatever superimposed on it. The perfect uniformity and continuity of this spectrum make it the best background for the examination of absorption spectra (for example, of benzene) in the ultra-violet. Helium and neon give similar, although less intense, continuous spectra extending far into the ultra-violet. A. A. E.

**Identification of Air Lines in Spark Spectra from λ 5927 to λ 8683.** PAUL W. MERRILL, F. L. HOPPER, and CLYDE R. KEITH (*Astrophys. J.*, 1921, **54**, 76—77).—Data have been secured (cf. *ibid.*, 1920, **51**, 211) for the chemical identification of the air lines from λ 5927 to λ 8683 in spark spectra. The spark was operated alternately in oxygen and air, and the lines due to oxygen identified. The remaining air lines, except a few argon lines, are ascribed to nitrogen. A. A. E.

**The Intensity Distribution in the β-Ray Spectra of Radium-*B* and -*C*.** J. CHADWICK and C. D. ELLIS (*Proc. Camb. Phil. Soc.*, 1922, **21**, 274—280).—Two radically different views of β-ray disintegration have been put forward. That of Meitner (this vol., ii, 416) in which the entire β-ray emission of a radioactive substance consists of a series of homogeneous groups of electrons, and that of Ellis (this vol., ii, 466) according to which the disintegration electrons form a continuous spectrum. In the present paper, measurements are made of the intensity distribution in the β-ray emission of radium-*B* and -*C*, and it is shown that the continuous spectrum has a real existence, and is independent of the experimental arrangement. The five strong lines in the radium-*B* β-ray spectrum formed only one-fifth of the total emission,

the main feature of which was the continuous spectrum. The number of electrons received per second in the ionisation chamber, calculated from the observed ionisation currents, was in agreement with the number of atoms disintegrating per second at the source.

W. E. G.

**The Spectrum of Radium Emanation.** R. E. NYSWANDER, S. C. LIND, and R. B. MOORE (*Astrophys. J.*, 1921, **54**, 285—292).—Photographic and visual measurements were made of the spectrum of radium emanation, λλ 3982 to 7450. The relative intensities of the lines differed markedly, as a rule, from the previous observations of Watson and Royds and Rutherford; many strong lines of the one hundred and twenty previously measured were not found; of the forty-four lines obtained, nine were new. Changes of intensity with duration of the discharge were observed, some lines decreasing and some increasing in strength, whilst the colour of the discharge changed from a bright glow to violet. A modification is described of Duane's apparatus for the purification of radium emanation. A. A. E.

**The Spectrum of Neutral Helium.** C. V. RAMAN (*Nature*, 1922, **110**, 700—701).—A criticism of Silberstein's attempt (this vol., ii, 674) to explain the spectrum of neutral helium on the assumption of the independence of the electrons. The view is expressed that the approximate agreements between the calculated and actual frequencies are merely fortuitous arithmetical coincidences, and a number of statements are made, based on a survey of the figures and a series of computations, in its support. The same considerations apply with even greater force in the case of lithium, when a choice of six numbers, compared with four in the case of helium, is permitted. Further, it is held that the Rydberg constant 109723 is appropriate only to the case of the ionised helium atom in which only one electron is coupled to the nucleus.

A. A. E.

**The Structure of the Red Lithium Line.** T. R. MERTON (*Nature*, 1922, **110**, 632).—A criticism of the views of McLennan and Ainslie (this vol., ii, 541; cf. Zeeman, A., 1913, ii, 812; *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1130; Kent, *Astrophys. J.*, 1914, **40**, 337; King, *ibid.*, 1916, **44**, 169; Takamine and Yamada, *Proc. Tokio Math. Phys. Soc.*, 1914, **7**, 339; Merton, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 101) on the structure of the lithium line $\lambda = 6708$. Under the appropriate conditions, the line appears to be a simple pair; if the four components were really two pairs due to the two isotopes, they should always appear together with an invariable intensity ratio of 1 : 16. This is not in accordance with the experimental results. Theoretical objections are also raised. A. A. E.

**The Exploded-wire Spectrum of Calcium.** R. A. SAWYER and A. L. BECKER (*Physical Rev.*, 1921, **18**, 164).—By expending constant power on wires of varying mass of calcium and other elements, or varying power on wires of constant mass, spectra

have been obtained in which the relative intensities of the three calcium lines, *H*, *K*, and λ 4227, vary as in the spectra of stars of different classes. The calcium lines, particularly *H* and *K*, appear to be tremendously enhanced by the very high temperature of the explosion, since they appear more prominently in the spectra of exploded wires of other metals (in which the amount of calcium present must be very minute) than the spectra of the metals themselves. A. A. E.

**Excitation of Atoms to Light Emission by Electron Collisions.** R. SEELIGER (*Z. Physik*, 1922, **11**, 197—200).—According to the Bohr theory, the passage of an electron from an initial to a final orbit is determined by the two probabilities, *W* and *w*, where *W* is the probability that the electron shall be raised from the normal to the initial orbit, and *w* is the probability of the transition from the initial to the final state. The former (*W*) is affected by the conditions of excitation, and according to Franck, the latter (*w*) should be also dependent on the external conditions. To test this point, the effect of the velocity of the exciting electrons on the intensity of certain related mercury lines has been examined. Two pairs of lines, 4916 ($3{\cdot}5S—2P$) and 2857 ($3{\cdot}5S—2p_2$), and 2652 ($4d'—2p_2$) and 4339 ($4d'—2P$) were chosen, and the intensities of these measured in different parts of the glow-discharge. The form of the intensity curves were widely different for the individuals of both pairs, and the maxima occurred at different distances from the mercury electrode. Thus, in these cases, the probability of transition from one orbit to another is dependent on the external electric field. W. E. G.

**Mass-absorption Coefficients as a Function of Wave-length Above and Below the *K* X-Ray Limit of the Absorber.** F. K. RICHTMYER (*Physical Rev.*, 1921, **17**, 264—265).—An extension to silver and lead, and to longer wave-lengths, of the relation between *X*-ray wave-lengths and the mass-absorption coefficient $\mu/\rho$ (for aluminium, copper, and molybdenum, cf. this vol., ii, 105). A. A. E.

**The Evidence Regarding the so-called "*J*" Radiation in the Characteristic X-Ray Spectra of the Elements.** F. K. RICHTMYER (*Physical Rev.*, 1921, **17**, 433—434).—From an examination of the absorption of water, aluminium, copper, boron, silver, and molybdenum, the author concludes that, within 1%, there are no discontinuities in absorption suggestive of *J*-radiations. A. A. E.

**Absorption of X-Rays by Chromium, Manganese, and Iron.** WILLIAM DUANE and HUGO FRICKE (*Physical Rev.*, 1921, **17**, 529—531).—The *K* critical absorption wave-lengths ($\lambda \times 10^8$ cm.) of chromium, manganese, and iron are 2·0623, 1·8893, and 1·7377, respectively. The energy changes corresponding with the critical absorption appear to be the same for iron atoms in the bi- and tervalent conditions. A. A. E.

**The Tungsten X-Ray Spectrum with a Mica Spectrometer.** USABURO YOSHIDA and SHINSUKE TANAKA (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 173—178).—The arrangement is essentially that used previously (*ibid.*, 1921, **4**, 343) and the grating constant was calculated from the wave-lengths of the prominent lines of the *L*-series of tungsten. With the mica spectrometer the *X*-ray spectrum of tungsten may be obtained up to the seventh and even to the tenth order. Eleven lines of unknown origin were detected on the photographs, but these might be due to reflection from the mica in an unknown manner. The wave-lengths of the known lines are in agreement with those given by Siegbahn within the limit of the experimental error. The existence of the line found by Overn at 1070 Å. has been confirmed. W. E. G.

**Critical Potentials of the L-Series of Platinum.** DAVID L. WEBSTER (*Physical Rev.*, 1920, **15**, 238).—The *L*-series must be regarded as consisting of three sub-series, $L_1$ (containing the lines $l$, $\alpha_2$, $\alpha_1$, $\beta_2$, $\beta_5$, and $\beta_6$), $L_2$ (containing the lines $\eta$, $\beta_4$, $\beta_1$, $\gamma_1$, $\gamma_2$, and possibly $\beta_3$), and $L_3$ (containing the lines $\gamma_4$, $\gamma_3$, and possibly $\beta_3$). A. A. E.

**Temperature Shift in Near Ultra-red Bands.** H. M. RANDALL, W. F. COLBY, and R. F. PATON (*Physical Rev.*, 1920, **15**, 541—543; cf. Randall and Imes, A., 1920, ii, 570; Colby, A., 1920, ii, 655).—Curves are given showing the absorption of hydrogen chloride in the neighbourhood of 3·4 $\mu$ at 20°, 105°, and 250°. It appears that in spite of the outward shift of intensity to higher velocity values, no shift takes place in the fine structure. Further investigations at higher temperatures are in progress. A. A. E.

**The Labile Nature of the Halogen Atom in Organic Compounds. VII. Absorption Spectra of the Halogen Derivatives of some Cyclic Compounds, and their Bearing on the Question of an Oxygen-Halogen Linking.** HUGH GRAHAM and ALEXANDER KILLEN MACBETH (T., 1922, **121**, 2601—2608).

**Carbon Dioxide Absorption in the near Ultra-red.** E. F. BARKER (*Astrophys. J.*, 1922, **55**, 391—398).—New absorption curves have been obtained. The 2·7 $\mu$ region, previously considered to be a doublet, proves to be a pair of doublets, with centres at 2·694 $\mu$ and 2·767 $\mu$ (approx.). The 4·3 $\mu$ band appears as a single doublet with centre at 4·253 $\mu$. The frequency difference between maxima is nearly the same for each of the three doublets, and equal to $4 \cdot 5 \times 10^{11}$. Complete resolution of the band series was not effected, but there is evidently a complicated structure, with a "head" in each case on the side of shorter wave-lengths. If a linear configuration of the three atoms in the molecule of carbon dioxide is assumed, the moment of inertia of the molecule, computed from the doublet frequency difference, is $50 \times 10^{-40}$. This gives the distance of the central carbon atom from each oxygen atom as $0 \cdot 97 \times 10^{-8}$ cm. Since the linear molecule could have only three modes of vibration, it is suggested that the two doublets

at 2·7 $\mu$ may correspond with two successive changes in statio *state for the same vibration.* A. A. .

**Absorption of Light by Inorganic Salts.** E. F. GEC (*Diss., Ohio,* 1920).—The change in absorption produced by mi sulphates in solution with other sulphates is small in compai with corresponding changes in nitrates, and still smaller tha the case of chlorides. The influence of temperature on the abs tion of solutions of mixed salts is greatest with chlorides. therefore appears that Ostwald's view that the coloured ion a *is effective in the absorption of light is not well founded.* W the ratio of the absorption of the mixture to the sum of the abs tions of the component parts is plotted as a function of the w length, the resulting curve generally shows a minimum near middle of the spectrum. Many of the curves are shown t exponential in form. CHEMICAL ABSTRACT

**The Absorption Spectra of *o*-Cresolsulphonphthal** W. R. ORNDORFF, R. C. GIBBS, M. SCOTT, and S. D. JACE (*Physical Rev.,* 1921, **17**, 437).—*o*-Cresolsulphonphthalein and o related compounds have in neutral aqueous solutions two absorp bands which are modified or replaced by new bands on the addi of acid or alkali. In the case of a dilute alkaline solntion, the type of absorption is not stable, but reverts to the two band abs tion found in the corresponding neutral solution. It is consid that in neutral aqueous solutions the carbinol and hydrate fc of the phthalein are present and that on the addition of either or alkali a salt having a quinoid structure is formed. A. A.

**Flame Excitation of Luminescence.** E. L. NICHOLS D. T. WILBER (*Physical Rev.,* 1921, **17**, 453—468).—The fluoresc developed by certain substances, notably lime, zirconia, magn silica, alumina, zinc oxide, some phosphorescent sulphides, a number of other compounds, by contact with a hydrogen fl differs from photoluminescence and from mere temperature radia A definite temperature-range exists for each substance, and effect does not appear to depend on the presence of traces of a ating elements. Many substances which are strongly lumines under the action of light do not respond to flame excitation. E ation does not occur by heating in air or hydrogen or in a vacu or by contact with a jet of hydrogen while hot unless the hydr is ignited and conditions are favourable for free oxidation. effect probably cannot be ascribed to the presence of H or molecules. The spectra obtained by flame excitation have examined. A. A.

**Chemoluminescence. I.** A. A. GRINBERG (*J. Russ. P Chem. Soc.,* 1920, **52**, 151—185).—A summary is given of prev work on this subject, particularly on bioluminescence (cf. Ra zewski, A., 1877, ii, 345; Lenard and Wolf, A., 1888, 1000; Tra A., 1905, ii, 662; Trautz and Schorigin, A., 1905, ii, 494; Du A., 1913, i, 1021; Harvey, A., 1917, i, 365; ii, 436; Goss, 1917, ii, 436). The light effect obtained with the system, p

gallol–hydrogen peroxide–potassium permanganate under various conditions has been investigated, the intensity of the light being measured photographically. At 16—17° the greatest intensity was obtained with a mixture of 4 c.c. of 0·005*M*-potassium permanganate, 2 c.c. of 0·01*M*-pyrogallol, and 2 c.c. of 3—12% hydrogen peroxide solutions. Sulphuric acid in the concentration 0·018—0·04% weakens the effect considerably, whilst 0·0046—0·026% of potassium hydroxide enhances it to a slight extent. T. H. P.

**Mutarotation. I.** C. N. RIIBER (*Ber.*, 1922, **55**, [*B*], 3132—3143).—The data with regard to the relationship of mutarotation to other physical changes in solution are very scanty and exhibit considerable discrepancies among themselves. The changes in refractive index and volume of a solution containing a substance undergoing mutarotation have now been studied.

The index of refraction of an aqueous solution of dextrose does not appear to vary when the ordinary Pulfrich refractometer is used, but the instrument is scarcely suitable for the purpose owing to the impossibility of maintaining the requisite degree of constancy in temperature. By means of a Hallwachs's prism, it can, however, be shown that the refractive index increases slightly with age in the case of dextrose solutions and that the change occurs with immeasurably greater rapidity when a little ammonia is added to the solution. The method, however, does not lend itself to the periodical observation of the action and attention has therefore been directed to the measurements of alteration of volume in the solution. The dilatometer employed resembles essentially a Sprengel pyknometer. One tube is firmly closed by a small rubber plate and the change in volume of the solution is indicated by the movement of the meniscus in the other limb and measured by means of a microscope. A movement of 0·005 mm. can be detected with certainty; this corresponds with an alteration in volume of less than 0·0000001. The capacity of the instrument is 66·7 c.c. The temperature is maintained constant to within 0·001°. It is thus shown that solutions of dextrose in water increase in volume during the process of mutarotation at a rate corresponding with that required for a unimolecular, irreversible reaction but subsequent observations prove that in reality a state of equilibrium is finally attained and indicate that water possibly takes some part in the change. The quantitative parallelism between mutarotation and change of volume makes it certain that the two phenomena have a common cause.

A solution of lactose the optical activity of which diminishes progressively shows a gradual expansion, whereas a contraction is observed with a solution of maltose with increase of specific rotation. Galactose solution suffers a primary expansion and a subsequent contraction. Solutions of sucrose and mannitol which do not exhibit mutarotation are constant in volume. Solutions of the optically inactive dulcitol do not undergo change in volume. Acetaldehyde, in 30 per cent. aqueous solution, exhibits a considerable expansion, whereas acetone under similar conditions gives

a marked and rapid contraction. Ethyl alcohol gives a slight expansion.

The applicability of the dilatometer just described is not restricted to reactions involving mutarotation, but since changes in volume are probably involved in all chemical reactions, it can be used for the investigation of processes taking place at the ordinary temperature. The accuracy of the procedure is at least as great as that of the polarimetric or refractometric method and it has the great advantage that it does not necessitate the use of transparent and colourless solution. It bas been found very useful in the study of the inversion of sugar by invertin and the saccharification of starch by ptyalin; in each case a marked contraction takes place as is to be expected. H. W.

**Photochemistry of Chlorine Detonating Gas.** FRITZ WEIGERT and KARL KELLERMANN (*Sitzungsber. Preuss. Akad. Wiss. Berlin,* 1922, **24**, 315—320).—The early stages of the combination of hydrogen and chlorine have been investigated. It is shown that a characteristic streaky appearance is visible in the gas mixture during the time 1/100—1/20 second from the moment of excitation. A vanishingly small quantity of hydrogen chloride only is formed directly by the radiation, but this is followed by a large subsequent formation. From this result, the authors show that the primary reaction, contrary to many previous assertions, in all probability is in keeping with Einstein's photochemical equivalent law. J. F. S.

**Photochemical Oxidation of Hydriodic Acid.** CHR. WINTHER (*K. Danske Vid. Medd. Math.-fys. Medd.*, 1920, **2**, No. 2, 1—28; from *Chem. Zentr.*, 1922, iii, 592).—In the oxidation of hydriodic acid solutions in thin films, the velocity of reaction was measured at the beginning and also in the course of the reaction. The effect of shaking, oxygen concentration, and wave-length of light was also investigated. With vigorous shaking, the reaction shows an increase in velocity during an induction period and then remains constant. The sensitiveness of the oxidative process to light is proportional to the absorption of tri-iodide-ion which acts as an optical catalyst. This is an example of "optical autosensibilisation" where the catalyst is actually formed by the reaction which it catalyses. The oxidation of leuco-compounds to dyes, the oxidation of pyrogallol in alkaline solution, and the oxidation of sodium sulphide in aqueous solution are similarly catalysed.

G. W. R.

**Photochemical Efficiency of Absorbed Radiation.** CHR. WINTHER (*K. Danske Vid. Medd. Math.-fys. Medd.*, 1920, **2**, No. 3, 1—35; from *Chem. Zentr.*, 1922, iii, 592—593).—The amount of energy absorbed in the photochemical oxidation of a certain amount of hydrogen iodide was found to be identical with the amount calculated as necessary for its activation. The absorbed energy is thus used exclusively for the activation of the hydrogen iodide molecule. The equivalence of absorbed energy and energy required

r activation is enunciated as a general principle in photochemical actions. Certain consequences of this principle are discussed. iscrepancies are attributed to experimental errors or to the con- rsion of the absorbed radiation into radiation of shorter wave- ngth. G. W. R.

**The Decomposition of Hydrogen Molecules by Excited ercury Atoms.** G. CARIO and J. FRANCK (*Z. Physik*, 1922, l, 161—166).—On the collision of excited atoms with other atoms, e quantum energy may be given up without light emission (cf. ranck, this vol., ii, 464), and chemical change may take place. n exposing a mixture of hydrogen and mercury to the mercury ie 2536·7 Å., the radiation was strongly absorbed, and the hydrogen ssociated. Powdered copper oxide was reduced, and the pressure the hydrogen continuously decreased at a temperature of 45°. ı the absence of hydrogen and mercury, no reduction occurred. ie mercury is acting as a sensitiser. In the absence of copper ide, the atomic hydrogen is adsorbed by the walls. At low essures, the velocity of dissociation was very slow, and this haviour indicates a short period of activity of the mercury atoms. he velocity of reaction increases up to 15 mm. pressure and then mains constant. Tungsten trioxide is also reduced, and the duction is not in any way due to illumination by the light. nce tungsten oxide is not reduced by hydrogen below a red heat, is unlikely that the phenomenon is caused by rapidly moving drogen molecules.

The hydrogen is dissociated by mercury atoms which are in the $)_2$ condition. Calculations show that the upper limit for the at of dissociation of hydrogen is 112 Cal. W. E. G.

**Photoelectric Effect of Alkali [Metal] Vapours and a New etermination of *h*.** E. H. WILLIAMS and JAKOB KUNZ 'hysical Rev., 1920, **15**, 550).—The resonance potential of cæsium ıpour is 1·48 volts, whilst the ionisation potential is 3·9 volts. the same amount of work is required for the breaking up of a utral cæsium atom by light as by moving electrons, then the ng wave-length limit of the photoelectric effect of cæsium vapour ould be $l=318{\cdot}4$ μμ, according to the equation $hn=eV$. If this found to be the case, then (1) the long wave-length limit is quite fferent for cæsium metal and for cæsium vapour, and (2) a new iotoelectric method for the determination of *h* is available. xperimentally, there is no photoelectric effect in cæsium vapour own to 313 μμ, but the effect at 253 μμ is very marked.

A. A. E.

**The Photoelectric Long Wave-length Limit of Platinum id Silver.** OTTO STUHLMAN, jun. (*Physical Rev.*, 1920, **15**, 19—550; cf. *ibid.*, 1919, **13**, 109).—The photoelectric long wave- ngth limits of platinum and silver are $\lambda_0=284$ μμ and $\lambda_0=325$ μμ, spectively. A. A. E.

**Soft X-Rays of Characteristic Type.** E. H. KURTH (*Physical ev.*, 1921, **17**, 528—529; **18**, 99—100).—The radiation curve of

aluminium shows breaks at 38 and 120 volts, corresponding with 326 Å.U. (possibly the $M$-series) and 103 Å.U. (possibly the $L$-series), respectively. For iron, 62·8 Å.U. and 48·4 Å.U. appear to represent the extremes of the $M$-series, whilst 16·3 Å.U. probably corresponds with the $L$-series. There was also some indication of a break in the curve at 50 volts, corresponding with 247 Å.U. Carbon yields a pronounced break at 43·6 Å.U., agreeing with the extrapolated value for the $K$ series. The following approximate figures (Å.U.) are also recorded: $K$-series: carbon, 42·6; oxygen, 23·8. $L$-series: carbon, 375; oxygen, 248; iron, 16·3; copper, 12·3. $M$-series: iron, 54·3; copper, 41·6. $N$-series: iron, 247; copper, 119. A. A. E.

**Absorption of X-Rays in Crystals.** TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 10, 1—6).—It has been shown in a previous paper (A., 1921, ii, 367) that, in the case of amorphous substances, the molecular absorption coefficient can be calculated as a sum of the atomic absorption coefficients for $X$-rays of the constituent elements. It is now shown that the same holds true for a number of crystalline substances, including alum, calcite, and gypsum. The observed absorption coefficients agreed with considerable accuracy with those calculated from the atomic absorption coefficients derived from a study of amorphous substances, and the absorption showed no variation in different directions in the crystals. In the cases of rock salt and sylvine an abnormally low absorption was observed when the incident rays were parallel to the principal planes of the crystal. This effect, which is probably due to scattering, becomes less marked as the angle between the direction of the incident rays and the principal structural planes is increased. E. H. R.

**The Durability of Radium Solutions.** AUG. BECKER (*Z. anorg. Chem.*, 1922, **124**, 143—152).—The permanency of the radium solution is defined as its constancy in emitting emanation. The author found that solutions containing from 0·02 to 0·0000005 mg. radium per gram solvent did not show any decay in eight years. The possible experimental error was 1%. W. T.

**Electric Furnace Experiments involving Ionisation Phenomena.** ARTHUR S. KING (*Astrophys. J.*, 1922, **55**, 380—390; cf. Saha, A., 1920, ii, 457, 659; 1921, ii, 4, 162; *Proc. Roy. Soc.*, 1921, [*A*], **99**, 135).—Results are obtained which verify certain predictions due to Saha. It is shown that the intensity of the enhanced lines of alkaline-earth metals is decreased by the presence of the more easily ionised potassium and cæsium. The results with mixed gases are such as would be expected if it is assumed, with Saha, that flame and enhanced lines are associated with neutral and ionised atoms, respectively. A. A. E.

**Thermal Ionisation of Gaseous Elements at High Temperatures. Confirmation of Saha's Theory.** ARTHUR A. NOYES and H. A. WILSON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 303—307).—On the basis of Saha's hypothesis (A., 1920, ii, 659; 1921,

ii, 162), the authors show that the constant, $K$, of the reaction $M = M^+ + E^-$ can be calculated by means of the formula $\log k = -5048V/T + 2{\cdot}5 \log T - 6{\cdot}56$, where $V$ is the ionisation potential and $T$ the absolute temperature. From some earlier experiments of Wilson on the conductivity of salts in flames, it is possihle to calculate approximately the value of $K$ (A., 1916, ii, 72). These values have been calculated for the case of salts of the alkali metals and the value of $K \times 10^{12}$ obtained both by means of the above formula and Wilson's experiments. The values in brackets are obtained by the formula, cæsium 3500 (8200), rubidium 780 (1600), potassium 430 (620), sodium 5·6 (6·2), and lithium 0·8 (1·4). The two sets of values are comparable and of the same order, and this is taken as a confirmation of Saha's hypothesis. From these ionisation constants, it is possible to calculate the degree of ionisation of an element into an electron and an ion. J. F. S.

**Resonance and Ionisation Potentials of Helium.** J. Franck (*Z. Physik.*, 1922, **11**, 155—160).—A theoretical paper. The lines in the parhelium spectrum discovered by Lyman (this vol., ii, 674) throw light on the relationship between the resonance and ionisation potentials, and the structure of the helium atom. The potentials calculated from the lines in this spectrum are in agreement with the experimental results of Franck and Knipping (A., 1920, ii, 72) and Horton and Davies (A., 1921, ii, 672), if 0·8 volt be subtracted from these values. It is not possible that this divergence is due to error of observation. Reasons are advanced to show that the first break in the curve corresponds with the change $0{\cdot}5S - 1{\cdot}5s$, and the second with two successive changes, $0{\cdot}5S - 1{\cdot}5S + 0{\cdot}5S - 1{\cdot}5s$. The difference is $0{\cdot}5S - 1{\cdot}5S$, and not $0{\cdot}5S - 1{\cdot}5s$ as has been assumed. This accounts for the difference of 0·8 volt.

The resonance and ionisation potentials of other gases, which are based on those of helium, must be reduced by this amount, and the following ionisation potentials are obtained after making this correction: $H_2$, 16·4±0·25, 29·7±0·4; $N_2$, 17·05±0·3, 24·7, 30·0; HI, 12·7; HBr, 13·3; HCl, 13·7; HCN, 14·8. W. E. G.

**Spectroscopic Investigation of the Ionisation of Argon by Electron Collisions.** F. Horton and Ann Catherine Davies (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 131—150).—The authors' previous determinations of the resonance radiation, 11·5 volts, and ionisation, 15·1 volts, of argon (cf. A., 1920, ii, 215) have been confirmed by both spectroscopic investigation and current-voltage curves. The apparatus used resembles that developed in their experiments with neon (cf. A., 1921, ii, 422). The brighter red lines of the argon spectrum appeared simultaneously, at a point a few volts higher than the ionisation voltage. The first visibility of the lines is accompanied by a sharp increase in the current which is due to the neutralisation of the space charge of the emitted electrons near the filament. On reducing the voltage the lines persist to an extent which depends on the electron current. At moderate gas pressures, the difference between the voltages of

appearance and disappearance of the lines sometimes amounted to 11 volts. On decreasing the voltage from about 25 volts, the lines in the "red spectrum," λ 4510·9, λ 4345·3, λ 4272·3, undergo a marked enhancement in the region of 19 to 16 volts. The intensity of the bright lines λ 7067·5 and λ 6965·8 decreases continuously in brigbtness as the voltage is lowered. The "blue spectrum" requires for its stimulation higher potential differences across the tube. At 19 volts, the lines λ 4430·4 and λ 4426·2 become visible, and with increasing voltage the intensity increases up to 24 volts and remains stationary until 34 volts, when the intensity again rapidly increases. The break at 19 volts corresponds with the removal of a second electron from an already ionised atom, and that at 34 volts with the double ionising voltage of the argon atom. The difference between the two values gives the normal ionising voltage. From a consideration of the minimum voltages at which the "blue spectrum" lines could be detected, it is shown that the Stark classification of the helium lines into "bivalent" and "tervalent" is inaccurate. The ionisation voltage is related to one of the *M X*-ray absorption limits of the elements in a manner analogous to that in which the helium ionisation voltage is related to the *K* absorption limits, and the neon ionisation voltage to the *L* absorption limits. W. E. G.

**Luminous Discharge in Hydrogen and Mercury and a New Method of Measuring Ionisation Potentials.** GEORGE E. GIBSON and W. ALBERT NOYES, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 2091—2106).—The authors have examined the conditions of stability of the luminous discharge in hydrogen and mercury, and the variation of the potential, $E_d$, at which the luminous discharge vanishes, with changes of pressure. To explain the phenomena observed, they put forward the hypothesis that the potential gradient in the portion of the tube between the cathode and the place where ionisation first occurs diminishes as the pressure is decreased until at the minimum of $E_d$ the potential drop in this region has fallen to a very low value, not more than a few tenths of a volt in the shorter tubes or more than about a volt in the longest tubes measured. At the higher pressures, ionisation occurs at regions intermediate in position between the anode and cathode and as the pressure is diminished these regions recede from the cathode until at the minimum of $E_d$ ionisation occurs only in the immediate neighbourhood of the anode. It is shown that the voltage at which the luminous discharge in hydrogen disappears in tubes furnished with heated tungsten cathodes is a function of the pressure for a given tube passing through a minimum value which is usually a simple multiple of the ionisation potential, 30·9±0·4 volts. In mercury vapour the disappearance voltage of the luminous discharge is a simple integral multiple of the ionisation potential, 10·7±0·4 volts. J. F. S.

**Electrical Conductivity of Hydrochloric Acid and Potassium Chloride in Presence of Sucrose.** ARTHUR JOSEPH KIERAN (*Trans. Faraday Soc.*, 1922, **18**, 119—125).—Experimental deter-

minations have been made of the electrical conductivities at 25° of solutions of hydrochloric acid of concentrations ranging from 0·05*N* to 0·0005*N* in the presence of 5%, 10%, and 20% of sucrose. Similar determinations were made with potassium chloride solutions ranging from 0·01*N* to 0·0005*N* in the presence of 10% of sucrose. In the latter case, the equivalent conductivity increased normally with increasing dilution, to an asymptotic limit. In the case of hydrochloric acid solutions, however, the behaviour was abnormal, the equivalent conductivity passing through a maximum in the region *N*/300—*N*/500, dependent on the concentration of the sucrose, and thereafter steadily decreasing with increasing dilution. This abnormality was traced to the presence of minute traces of an electrolytic impurity (probably an organic salt of calcium) in all samples of sucrose. Values of $m$ in the relation $\Lambda=\Lambda'\eta^m$, in which $\Lambda$ and $\Lambda'$ are respectively the equivalent conductivities in media of unit viscosity and of viscosity $\eta$, have been determined as follows: hydrochloric acid and sucrose, 0·57; hydrochloric acid and dextrose, 0·68; potassium chloride and sucrose, dextrose, and glycerol, respectively, 0·73, 0·77, and 0·92. The results confirm the conclusion of Kraus (A., 1914, ii, 90) that $m$ approaches the value unity as the molecules of the medium become smaller in size and the larger the size of the ions of the electrolyte.

J. S. G. T.

**Conductivity of Sodium Iodide in Amyl Alcohol at very Low Concentrations.** CHARLES A. KRAUS and J. EGBERT BISHOP (*J. Amer. Chem. Soc.*, 1922, **44**, 2206—2212).—Exceedingly pure amyl alcohol may be prepared, as follows: ordinary amyl alcohol was submitted to an initial fractionation and the portion boiling above 130° dehydrated over quicklime, after which it was redistilled. The product was treated with a small amount of sodium and the resulting solution repeated fractionated. In this way, amyl alcohol with a specific conductivity of $2\times10^{-8}$ was obtained and by effecting the fractionation under reduced pressure the specific conductivity became $1\times10^{-8}$. Solutions made up in this product were not stable, but if the alcohol was subjected to fractional condensation under reduced pressure and the distillate collected in the conductivity cell a product with specific conductivity $1{\cdot}4\times10^{-9}$ was obtained and solutions made up in this were very stable; solutions of sodium iodide in this specially prepared amyl alcohol did not vary more than 0·1% in fourteen hours. The electrical conductivity of solutions of sodium iodide in amyl alcohol was measured at 18° for concentrations ranging between $1{\cdot}0\times10^{-5}N$ to $17\times10^{-5}N$. The mean variation of the results does not exceed 0·1%. In the more dilute solutions, the points conform to the requirements of the law of mass action within the limits of the experimental error. At the higher concentrations there is a small although constant deviation from the mass action relation. From an extrapolation of the curve to zero concentration the value 11·059 is obtained for $\Lambda_0$ and the value $2{\cdot}933\times10^{-4}$ for $K$.

J. F. S.

**Variation of the Electrical Conductivity among the Ammoniacal Derivatives of Platinous Nitrite.** L. A. TSCHUGAEV and N. A. VLADIMIROV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 135—138).—The values of $\Lambda_{1000}$ for tetra-amminoplatinous nitrite, $[Pt4NH_3](NO_2)_2$; nitrotriamminoplatinous nitrite,

$$[NO_2Pt3NH_3]NO_2;$$

*cis-* and *trans*-dinitrodiamminoplatinum, $[(NO_2)_2Pt(NH_3)_2]$; and potassium platinonitrite are found to be, respectively, 276·5, 96·5, 0·95, 2·42, and 302·4. The observed value of $\Lambda_{2000}$ for nitrotriamminoplatinous platinonitrite, $[NO_2Pt3NH_3]_2Pt(NO_2)_4$, is 217, the value calculated by summation of the mobilities of the corresponding ions being 197·2 (cf. Tschugaev and Kiltinovitsch, T., 1916, **109**, 1286). T. H. P.

**Passivity and Over-potential.** ULICK R. EVANS (*Trans. Faraday Soc.*, 1922, **18**, 1—13).—It is suggested that the relative values of the interfacial tensions between the metal, corrosion product, and solution is the factor on which the protection against corrosion of the metal by the solution depends. The activation of passive metals by chlorides is related to the peptising action of metallic hydroxides by chlorides; the rendering passive by chromates is correlated with the flocculating action of these salts. The protective layer probably consists of a layer of oxygen atoms connecting the metal on the one side with solution on the other. Similarly, at a cathodically polarised electrode a layer of hydrogen nuclei connect the metal with the liquid, the hydrogen being probably in a state intermediate between the elementary and ionic forms. The theory is, in some respects, opposed to that of Friend (T., 1922, **119**, 932). J. S. G. T.

**Chemical Passivity of Metals.** J. GILLIS (*Natuurwetenschapp. Tijdschr.*, 1921, **3**, 66—68).—The phenomena of passivity may not be explained by the formation of an oxide membrane protecting the metal. The most accurate optical methods—which permit estimation of a layer of 0·8 $\mu\mu$—fail to detect any sign of an oxide membrane. On the other hand, the metals which become passive by anodic polarisation are also those the ions of which do not readily discharge and precipitate on the cathode. There is, therefore, a co-existence of the anodic retardation (passivity) and of the cathodic retardation (slow metallic precipitation); the transformation $M^+ \rightleftarrows M + \oplus$ is slow in both directions.

CHEMICAL ABSTRACTS.

**Thermo-electric Force, the Entropy of Electrons and the Specific Heat of Metals at High Temperatures.** WENDELL M. LATIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 2136—2147).—A theoretical paper in which the thermo-electric force of a circuit of two metals has been expressed in terms of the entropy of the electrons in the two metals. This expression has the form

$$dE/dT = \int_0^T \sigma_2 \,.\, dT/T - \int_0^T \sigma_1 \,.\, dT/T$$

$\sigma_1$ and $\sigma_2$ are the specific heats of the electrons of the two

metals. It has been postulated that the specific heat of a gram-molecule of electrons in a metal is given by the increase in the specific heat at constant volume of a gram-molecule of the meta[l] above the equipartition value of $6/2R$. On this assumption, th[e] absolute value of the thermo-electric force of the potassium sodiu[m] couple has been calculated at 25° from values of the specific heat[s] of these metals. The changes in thermo-electric force of platinum iron, cobalt, nickel, gold, copper, tungsten, molybdenum, calcium aluminium, magnesium, and lead against silver have been calculate[d] from specific heat data for temperature differences of 100° to 700° Satisfactory agreement is obtained between the calculated an[d] observed values. To make these calculations, the existing dat[a] on the thermo-electric force have been collected; new data fo[r] the thermo-electric force of lead, zinc, magnesium, aluminium molybdenum, and tungsten against silver have been obtained and these are summarised in a thermo-electric diagram. Th[e] entropy of the metal electrons at low temperatures has bee[n] discussed and the possibility of using thermo-electric data a[s] a means of determining $C_v$ for metals at higher temperature pointed out. The $C_v$ curves for cobalt, iron, calcium, nickel palladium, aluminium, platinum, lead, magnesium, iridium, gold copper, silver, molybdenum, and tungsten have been drawn i[n] agreement with existing thermo-electric data. J. F. S.

**Thermochemistry and Electromotive Force in Electri[c] Elements.** JARL A. WASASTJERNA (*Monograph, Helsingfor[s]* 1918).—*A systematic, mathematical study of representative typ[es]* of electrolytic cells, the *E.M.F.* being derived from the reactio[n] energy and the affinity. The following results are recorded f[or] the various cells, for the reaction energy, $U$, the affinity, $A$, an[d] the electromotive force, $E$, respectively, the subscript figur[es] representing absolute temperatures: (1) Cu|saturated solutio[n] CuI|I crystals; $U_0$ 16296; $A_{293}$ 15908; $E_{293}$ 0·69. (2) Cd|satu[r]ated solution CdI,—$Hg_2I_2$ paste|Hg; $U_0$ 20856; $A_{294}$ 2048[5] $E$ 0·45. (3) Cu amalgam 10%|saturated solution $CuSO_4,5H_2O$,-$Hg_2SO_4$ paste|Hg; $U_{293}$ 25745; $A_{293}$ 16560; $E_{293}$ 0·353. ([4]) $H_2$|0·1$N$-HCl|$Cl_2$; $E_{298}$ 1·38. (5) Pb|saturated solution $PbCl_2$|$Cl_2$ $E_{291}$ 1·58. (6) $H_2$|equivalent weights of $FeCl_3$ and $FeCl_2$ i[n] 0·1$N$-HCl|Pt; $A$ 3480 and 5220; $E_{293}$ 0·42 and 0·46. ([7]) Daniell element with saturated solutions of $CuSO_4,5H_2O$ an[d] $ZnSO_4,7H_2O$; $U_{291}$ 52045; $A_{291}$ 49488 (subtract 220 cal. f[or] osmotic work); $E_{291}$ 1·69. (8) Daniell element with water [+] $100H_2O$; $U_0$ 50350; $A_{290}$ 50600; $E$ 1·098. Cells delivering electric energy, *but without thermal changes, are considered, but no da[ta]* are given. Values obtained for the Clark element are: $U_0$ 6731[6] $A_{288}$ 66218 (subtract 295 cal. for osmotic work); $E_{288}$ 1·43.

CHEMICAL ABSTRACTS.

**Complex Ion Formation in Hydrochloric Acid.** RAL[PH] M. HIXON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 1[,] 1—8).—If complex acids of the type $H_2CaCl_4$ exist in solutions [of] metallic chlorides in hydrochloric acid solution, a study of t[he]

migration of the metallic ion when such solutions are electrolysed should reveal their presence. Solutions of magnesium, calcium, barium, and zinc chlorides at different concentrations in concentrated hydrochloric acid were electrolysed for six to eight hours at 12 volts, and samples of anolyte and catholyte were analysed. The solutions of magnesium and calcium chlorides both showed migration of the metal towards the anode at medium concentrations, but towards the cathode at higher and lower concentrations. The migration towards the anode is strong evidence for the existence of complex ions of the type $(CaCl_2)_yCl_x^-$. The observed migration will depend on the relative concentrations of these complex ions and of the simple ions $Ca^{++}$, as well as on their migration velocities. At low concentrations, $Ca^{++}$ will predominate. At concentrations of $[CaCl_2]$ approaching saturation, $Ca^{++}$ may again predominate owing either to the decrease in the [HCl] concentration or to the formation of a more complex acid $(HCl)_x(CaCl_2)_y$ which would be less dissociated than the simpler acid formed at medium concentrations. E. H. R.

**The Hydration of the Lithium-ion.** J. Baborovsky and J. Velisek (*Chem. Listy*, 1922, **16**, 250—256).—A new apparatus suitable for determining the transport numbers and hydration of ions, consists of two membranes of parchment paper separating the central portion of the solution from the anodic and cathodic portions and also of an arrangement whereby the anodic and cathodic vessels can be disconnected and weighed with their contents. The hydration of the lithium-ion was calculated from the change in weights and in concentrations of the solutions around the electrodes. The determination of the hydration of ions by this method is complicated by electro-osmosis. This the authors claim to have measured by replacing the two parchment paper membranes by a single membrane and estimating the differences in the concentration and specific gravity of the central portion after each experiment. The lithium-ion has one more molecule of water of hydration than the chlorine-ion. The transport number of lithium in a decinormal solution of its chloride is $0{\cdot}3128 \pm 0{\cdot}0048$. The authors propose that the hydration of ions should be expressed in terms relative to that of the hydrogen-ion (the most mobile of all) which would be put equal to zero. W. T.

**Electrolysis with Drops of Mercury as the Electrode.** J. Heyrovsky (*Chem. Listy*, 1922, **16**, 256—264).—To study the electrolysis of aqueous solutions of the alkali and alkaline-earth metals, the author employed drops of mercury as the electrode; the apparatus is figured. This enabled him to determine the exact course of the electrolysis. Electrolysis is produced when a certain *E.M.F.* is applied the value of which is characteristic of each salt and depends on the logarithm of the concentration. The rapid increase of the current is explained by a diffusion towards the interior of the drop of mercury of very dilute amalgams. This diffusion commences because the metal has not sufficient mercury for combination. The author calculated the potential at which

the kations deposit from their normal solutions on a mercury cathode: lithium, −2·023; sodium, −1·860; potassium, −1·883; rubidium, −1·796; cæsium, −1·837. The affinity of the metals for mercury is given by the difference between the characteristic potentials of polarised drops and the normal electrolytic potentials of the pure alkali metals. They were found to be lithium, 1·281; sodium, 1·138; potassium 1·325; rubidium, 1·409; cæsium, (1·50). W. T.

**Simultaneous Electrodeposition of Lead and Lead Dioxide.** M. G. Mellon and H. F. Reinhard (*Proc. Indiana Acad. Sci.*, 1921, 181—188).—The amounts of lead and lead dioxide deposited simultaneously on the cathode and anode respectively when a solution of lead nitrate is electrolysed under varying conditions are variable when free nitric acid is present, but for neutral solutions a fair constancy exists in the ratios for the amounts of each of the two deposits to that of the quantity of silver deposited in a coulometer in the circuit. The ratios of the anode and cathode deposits respectively to the lead equivalent of the silver were 1·0053 (alternatively, 0·990) and 0·9864. The cause of the inaccuracy has not been traced. Chemical Abstracts.

**Electrolytic Migration of Sodium through Glass.** M. Pirani and E. Lax (*Z. tech. Physik*, 1922, **3**, 232—235).—The film of water which persists inside an exhausted glass tube was removed by the migration of sodium ions through the glass. A tube shaped like a lamp bulb and containing a small tungsten wire was exhausted and immersed in molten sodium nitrate at 450°. The wire was heated to a high temperature and a potential of 200 volts was applied between the wire and the molten bath. Sodium ions migrated through the glass and a yellow luminescence was produced in the tube. The water film was displaced by this process and was attacked by the hot tungsten as evidenced by the formation of a film of blue tungsten trioxide on the tube.

Chemical Abstracts.

**Method of Maintaining Small Objects at any Temperature between −180° and +20°.** P. P. Cioffi and L. S. Taylor (*J. Opt. Soc. Amer.*, 1922, **6**, 906—909).—The object is placed within a double-walled vacuum tube through which a stream of cold air, produced by the evaporation of liquid air contained in a Dewar vessel, is maintained. The rate of evaporation is controlled by means of an electric heater immersed in the liquid air, and determines the temperature to which the object is subjected. If desired, the object may be placed beyond the splayed-out end of the vacuum tube and an unbroken stream of cold air caused to flow across it by suction across the gap between the end of this tube and the wide mouth of a second tube connected to a vacuum pump. The latter tube should have a diameter about double that of the former and its length should be about twice that of the gap. The Dewar flask is preferably unsilvered, and is charged with liquid air through a funnel extending almost to the bottom and

provided with a plug of glass wool for filtering out ice and solid carbon dioxide. Temperature regulation may be maintained constant to within about 4° for many hours. J. S. G. T.

**Heat of Evaporation.** W. Herz (*Z. anorg. Chem.*, 1922, **124**, 56—58).—Employing the values obtained by Young, the author finds that the quotients of heats of evaporation at equal fractions of the critical temperatures (on absolute scale) are fairly constant for the twenty-six organic compounds investigated. The quotient of latent heat of evaporation and absolute temperature is given for pentane at different temperatures, and remains fairly constant, 0·11—0·15, except in the neighbourhood of the critical temperature. The same was found to hold in the case of twenty-eight other organic compounds. Acetic acid is exceptional, this being probably due to association. W. T.

**The Form of the Vapour Pressure Curve at High Temperature. I. The Curve for Lead.** Christopher Kelk Ingold (T., 1922, **121**, 2419—2432).

**High Temperature Investigations. XV. The Vapour Pressure of the Alkali Fluorides.** Otto Ruff, Gerhard Schmidt, and Susanne Mugdan (*Z. anorg. Chem.*, 1922, **123**, 83—88).—The apparatus used was like that described by Ruff and Mugdan (A., 1921, ii, 485) except that iridium crucibles were employed. The results are given for the fluorides of sodium, lithium, potassium, rubidium, and cæsium. The latent heat of evaporation calculated by means of Liempt's equation (A., 1920, ii, 588) was found to be, LiF, 52·2 Cal.; NaF, 51·1 Cal.; KF, 44·7 Cal.; RbF, 40·4 Cal.; CsF, 33·6 Cal. The critical temperatures calculated by the relationship $T_c = 1{\cdot}55 T_{760}$ are LiF, 3010°; NaF, 3070°; KF, 2750°; RbF, 2600°; CsF, 2370°. W. T.

**Heats of Combustion and Energy of Dissociation.** Walter Hückel (*Ber.*, 1922, **55**, [*B*], 2839—2843).—A detailed criticism of the publications of von Weinberg on this subject (A., 1920, ii, 668, 669).

In the final tables given by von Weinberg, only the previously known data for HCl, HBr, and HI are independent of hypothesis. The values for the C—C, C—H, C=C, C≡C, C—Cl, C—Br, and C—I linkings depend on the equality of $Q_{CC}$ and $Q_{CH}$ which has not been established. All the other data depend also on other unproved assumptions. The value of Weinberg's work lies in the fact that he has established for the first time a series of interesting relationships between the energy content of different organic compounds as illustrated by the scheme: (1) $Q_{(CO)} = Q_{C=O} + Q_{C-C}$, $Q_{(CO)} = Q_{C-O-C} + Q_{C-C}$, $Q_{C=O} = Q_{C-O-C}$ (2) $6Q_{NH} - Q_{N\equiv N} = 6Q_{CH} - 3Q_{CC}$ (3) $Q_{CC} - Q_{CH} = Q_{CCl} - Q_{HCl}$. H. W.

**The Energy of the Atomic Linkings in Diamond and in Aliphatic Hydrocarbons.** K. Fajans (*Ber.*, 1922, **55**, [*B*], 2826—2838; cf. A., 1920, ii, 354).—A reply to various criticisms

in many of which allowance has not been made for the admitted uncertainty of the author's data (cf. Hückel, A., 1920, i, 603; Polanyi, A., 1921, ii, 179; Swientoslawski, A., 1921, ii, 535; von Weinberg, A., 1920, ii, 668, 669; Thiel, A., 1920, ii, 667).

1. *Heat of sublimation of carbon and the absolute values of the linking energies.*—In the previous paper, the heat of sublimation of carbon was assumed for purposes of numerical illustration to be 287 Cal. Subsequently it has been shown by Kohn (A., 1921, ii, 302) that the heat of sublimation of carbon is 163·5 Cal. as a general mean of all measurements and that of diamond 168 Cal. The values for the most important linking energies have therefore been recalculated on a basis of 150 Cal. as the most probable value, on the supposition that carbon vapour is monatomic at 4200°, and that an equilibrium is established in Lummer's experiments.

2. *The energy of the double and triple linking.*—It is shown by a somewhat modified method that the heat of formation of a double or treble bond is greater than that of a single bond. Arguments are advanced in disproof of the criticism by Thiel (*loc. cit.*) that this conception is contrary to the known instability of substances with unsaturated linkings.

3. *Chemical forces in crystals.*—It has been asserted by Thiel (*loc. cit.*) that the chemical forces which are operative in the formation of a crystal are essentially those of subsidiary valency. This does not appear to be universally true, since the forces which hold the sodium chloride lattice together are identical with those which are operative in the vaporised salt molecule. The lattice is therefore held together by main valencies and the heat of sublimation is of the same order as that of the dissociation of the molecules into the free ions. On the other hand, the lattices of many organic compounds, for example solid hexane, are without doubt held together entirely by subsidiary valencies; this is shown by the fact that the molecular heat of sublimation of solid hexane is only 8 Cal., whereas the energy necessary for the disruption of the vaporised molecule into atoms is calculated to be 1511 Cal. The conception that the valency forces which unite the carbon atoms in the diamond lattice are identical with those uniting the carbon atoms of aliphatic compounds is not new; the advance made by Fajans consists in the exact quantitative demonstration of the correctness of the hypothesis by thermochemical methods.

4. The remainder of the communication is devoted to a question of priority (cf. von Weinberg, *loc. cit.*). H. W.

**The Thermochemistry of Carbon Compounds.** A. THIEL (*Ber.*, 1922, **55**, [*B*], 2844—2845).—A reply to Fajans (preceding abstract). H. W.

**Thermochemistry of Solutions.** M. LEVALT-EZERSKY (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 108—113).—Simple reasoning from fundamental principles leads to a number of equations which may be combined in the form: $q^l_m = q_m - Bq^l_l = BQ_l - Q_m = \phi_l - \phi_m = BR_l - R_m$, where $q^l_m$ represents the heat of dilution of a solution containing $100m/(100-m)$ grams of solute per 100 grams

of water to the concentration $l\%$, and $q_m^t$ and $q_l^t$ have analog significations; $Q_l$ and $Q_m$ are the heats of solution of $100l/(100-$ and $100m/(100-m)$ grams, respectively, of the solute in 100 gra of water; $\phi_m=Q_m$ and $\phi_l=m(100-l)Q_l/l(100-m)$, that is, $\phi_l-$ corresponds with the difference between the heats of solution one and the same quantity of the solute in such different amou of water that solutions of $l\%$ and $m\%$ concentration, respective are obtained; $R_l$ and $R_m$ represent, respectively, the heats reaction of $100l/(100-l)$ and $100m/(100-m)$ grams of the solu liquefied at the temperature of the experiment, with 100 grams water.

The above equation furnishes a convenient means of passi from the heats of solution of different amounts of a substance one and the same amount of solvent to the heats of solution one and the same quantity of solute in different quantities solvent and from these to the heats of dilution. T. H. P.

**Effect of Variation in Weight of the Riders and Plumm of the Westphal Balance on the Accuracy of Speci Gravity Determinations.** EDWARD A. TSCHUDY (*J. Am Chem. Soc.*, 1922, **44**, 2130—2135).—Accurate specific gravi determinations with the Westphal balance are possible only wh the weight of water displaced by the plummet at 15° and the weigh of the riders possess an exact multiple relationship amongst the selves. Variations in weight of the riders which disturb t relationship produce errors, often of considerable magnitude, specific gravity determinations. Inaccurate plummet therm meters are also a source of error. The magnitude of ordina variation in weight of riders and plummets has been ascertaine and equations have been derived for calculating the correcti which must be applied to any indicated balance reading to obta the true specific gravity of liquids lighter or heavier than wat Application of the corrections for any specific system of ride to indicated balance readings is facilitated by the construction a use of correction graphs. J. F. S.

**The Degree of Molecular Polymerisation of Substanc under Critical Conditions.** J. A. MULLER (*Compt. ren* 1922, **175**, 760—761).—A table of the calculated values of t degree of polymerisation of a number of elements and compoun under critical conditions is given. All the substances include with the exception of helium, undergo polymerisation to a certa extent; those which, under normal conditions of pressure a temperature, approximate in their behaviour to perfect gases a least affected, the values of the mean degree of polymerisati ranging from 1·227 in the case of hydrogen to 1·285 in that nitrogen. Liquid hydrocarbons and monohalogen derivatives benzene give values from 1·39 to 1·45, whilst those for esters saturated monobasic fatty acids vary from 1·45 to 1·48. Nitrile water, and acetic acid yield results in the neighbourhood of 2.

H. J. E.

**Corresponding States.** W. Herz (*Z. anorg. Chem.*, 1922, **123**, 132—136).—A theoretical paper in which the author investigates whether there is a constant relationship between the viscosity of liquids at the same fraction of the critical temperature. The viscosity at one-half the absolute critical temperature is divided by the viscosity at seven-twelfths the absolute critical temperature. In the case of 29 non-associating liquids, the ratio is 1·51—1·91. In the case of liquids which associate, the viscosity decreases more rapidly with increasing temperature and the ratio in the case of six liquids varies from 1·95 to 4·33. The author in the same way finds the ratio of the refractive indices at corresponding temperatures. The refractive index is calculated by equation $n=\sqrt{M+2dR_L/M-dR_L}$. In the case of 29 liquids the approximate constancy of the ratio showed the validity of the law of corresponding states. W. T.

**The Viscosity of Amphoteric Electrolytes in Solution.** Gunnar Hedestrand (*Z. anorg. Chem.*, 1922, **124**, 153—184).—Solutions of amino-acids are found to have a minimum viscosity at the isoelectric point. In the case of glycine and alanine, the viscosities of the anions is greater than that of the kations. Mixtures of glycine and alanine solutions have a viscosity which is the arithmetical mean of the corresponding unmixed solutions. The addition of neutral salts increases the viscosity of glycine and alanine solutions; it also displaces the minimum. The minimum viscosity of a gelatin solution is at the isoelectric point; the addition of salts increases the minimum value and at the same time shifts it to a lower hydrogen-ion concentration. On both sides of the minimum, the viscosity is decreased considerably by the salts. The author treated powdered gelatin with hydrochloric acid, and found that, on washing, a large amount of the gelatin went into solution; the same result was obtained by treating the powder with a mixture of hydrochloric acid and a salt.
W. T.

**Effect of Surface Tension.** P. B. Ganguly and B. C. Banerji (*Z. anorg. Chem.*, 1922, **124**, 140—142).—A stick of sodium hydroxide was held vertically in distilled water so that only one-half was immersed. In the absence of stirring, the part of the stick in contact with the surface dissolved the more rapidly. The same was observed in the case of sticks of potassium hydroxide, sodium nitrite, copper sulphate, and zinc chloride, and also of a zinc rod in dilute sulphuric acid. In the case of an iron rod in hydrochloric acid the reverse was observed and the part further from the surface dissolved the more rapidly. These effects are reduced by lowering the surface tension by a covering of oil, and are therefore assumed to be due to surface tension effects. W. T.

**Negative Adsorption. II. Calculation of the Amount of Adsorbed Solvent.** M. A. Rakusin and Tatjana Gönke (*Biochem. Z.*, 1922, **132**, 82—83).—The amount of adsorbed solvent

can be calculated by Gurvitsch's equation for positive adsorptior (A., 1914, ii, 435). H. K.

**The Sorption of Saturated Vapours by Charcoal.** JOHN DRIVER and JAMES BRIERLEY FIRTH (T., 1922, **121**, 2409—2414)

**Salt Adsorption on Metal Surfaces.** H. VON EULER and G. ZIMMERLUND (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 14, 1—23).—Measurements have been made of the silver nitrate and potassium chloride adsorbed from aqueous solution by finely divided gold particles and by gold leaf. It has been found that the amount adsorbed increases with the amount of salt in solution, at first linearly and then tending to a maximum. At the maximum there is more adsorbed than would correspond with a unimolecular layer on the gold. Experiments are also described with mercury dropping through a calomel solution in which the amount of mercury in solution was determined by finding its effect as an enzyme poison. W. O. K.

**Mordanting of Wool with Potash Alum.** W. W. PADDON (*J. Physical Chem.*, 1922, **26**, 790—793).—Experiments are described from which it is concluded that, contrary to the opinion of Knecht, the mordanting of wool with potash alum does not lead to the formation of definite chemical compounds on the fibre, but is strictly an absorption phenomenon in which both alumina and sulphuric acid are involved. J. S. G. T.

**Mordants. III. Chrome.** WILDER D. BANCROFT (*J. Physical Chem.*, 1922, **26**, 736—772).—The author reviews critically a part of the literature, more especially the work of Liechti and Hummel (*J. Soc. Chem. Ind.*, 1893, **12**, 244) concerned with the use of chromic oxide as a mordant in dyeing wool, cotton, and silk. The following are among the conclusions drawn: from dichromate solutions wool first adsorbs chromic acid and this is reduced to chromic oxide, which is the true mordant; within limits, increasing the acid concentration increases the chromic acid taken up; chromic acid oxidises organic compounds more readily in presence than in absence of wool; when wool is mordanted with chrome alum, a basic sulphate changing later to chromic oxide is first formed; silk adsorbs chromic oxide less strongly than wool does; cotton takes up scarcely any chromic oxide from chrome alum, but adsorbs it from an alkali solution; there is no evidence of the formation of any definite compound when wool is mordanted with chromic oxide. J. S. G. T.

**Tungsten Furnace for Experiments on Dissociation and Ionisation.** K. T. COMPTON (*J. Opt. Soc. Amer.*, 1922, **6**, 910—912).—Tungsten sheet is bent into the form of a cylindrical tube and clamped by end pieces each consisting of a steel ring fitting in a split rectangular steel block. The blocks are mounted on water-cooled brass tubes serving as leads for the heating current. Short glass tubes surround the leads for purposes of insulation. Loops of fine tungsten wire, drawn tightly round the cylindrical

tube, prevent bulging of the furnace. The central electrode consists of a straight length of "20 mil." tungsten wire welded to heavier molybdenum leads. A furnace 60 mm. overall length and about 5 mm. diameter was raised to a white heat by 100 amperes at 6 volts, and reached its melting point when a current of about 200 amperes was employed. J. S. G. T.

**The Thermal Decomposition of Chlorine.** FR. A. HENGLEIN (*Z. anorg. Chem.*, 1922, **123**, 137—165).—A description of the apparatus suitable for a reactive gas at low pressure and high temperature is given in detail (cf. this vol., ii, 441). The apparatus was tested by measuring the dissociation of bromine. The dissociation of chlorine was investigated at a pressure of $1\times10^{-5}$ atmospheres and between the temperatures of 700° and 900°. The following relationship was found to hold $\log K_{(atmos.)}=-(5400/4{\cdot}571T)+1{\cdot}75\ \log\ T-4{\cdot}09\times10^{-4}T+4{\cdot}726\times10^{-8}T^2+0{\cdot}93$ (cf. Bodenstein, A., 1916, ii, 554). The chemical constant of monatomic chlorine was calculated in three different ways: (1) by Stern's method (A., 1914, ii, 543), (2) by the reaction $Ag+\frac{1}{2}Cl_2=AgCl$, the heat effect and electromotive force of which are accurately known, (3) by the reaction $Hg+\frac{1}{2}Cl_2=HgCl$. The values found were respectively 0·68, 0·93, and 1·50. A linear relationship was found to exist between the heats of dissociation of chlorine, bromine, and iodine and their atomic radii and other spatial and thermal constants. The electroaffinity of chlorine was calculated to be 73 cal. W. T.

**Theory of Solvates.** JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 267—280).—Solvates in general and hydrates in particular vary in composition and are stable only within narrow limiting conditions, so tbat they must be regarded as transitory systems of physico-chemical character. The structure of a hydrate may be represented as a molecule of solute surrounded by an envelope of water molecules. Such of the latter as are near to the nucleus are held by a force approximating to chemical force, whereas the more remote, semi-combined water molecules exist under the configurational influences of chemical and kinetic forces, the system being in a condition of stationary thermal equilibrium. Hence it is possible for hydrates of different composition to exist in one and the same solution. This equilibrium of hydrates possesses a macroscopic character. The gradual variation of the thermal effect with the temperature confirms these views and distinguishes the decomposition of a hydrate from the stoicheiometric decomposition of an ordinary system. The existence of hydration is shown also by the change in the internal pressure, and the work of the internal forces may be expressed as the mechanical equivalent of chemical affinity (cf. Tammann, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907, **34**). T. H. P.

**Solubility of Carbon Dioxide and Nitrous Oxide in certain Solvents.** WILLIAM KUNERTH (*Physical Rev.*, 1922, **19**, 512—524).—In view of its bearing on the Lewis-Langmuir theory, a

comparison was made between the solubilities of carbon dioxide and of nitrous oxide between 18° and 36° in water, acetone, acetic acid, methyl alcohol, pyridine, ethyl alcohol, benzaldehyde, aniline, amyl acetate, ethylene bromide, *iso*amyl alcohol, and chloroform. In this series, the ratio of the solubility of carbon dioxide to that of nitrous oxide decreases regularly from 1·34 to 0·66. The ratio is nearly constant for each solvent, and the temperature coefficient, $ds/sdT$, which is always negative, is in most cases nearly the same for the two gases. It is found that Raoult's law does not hold for the solubility of gases in liquids, and that there is little, if any, relation between solubility and the difference between internal or cohesion pressures of solvent and solute. Since, however, the ratio of the solubilities of carbon dioxide and nitrous oxide (the former of which is the more active chemically, and therefore has the stronger polarity) varies regularly with the dielectric constant of the solvent, and since this constant may be taken as an index of the polarity of the solvent, it is suggested that polarity may be an important factor in determining the relative solubility of gases in liquids. The following figures, for carbon dioxide and nitrous oxide, respectively, at 20°, are abstracted from a table giving the solubilities expressed in c.c. of the gas under existing barometric pressure per c.c. of solvent: water, 0·900, 0·675; acetone, 6·98, 6·03; acetic acid, 5·23, 4·85; pyridine, 3·85, 3·58; methyl alcohol, 3·57, 3·32; ethyl alcohol, 2·87, 2·99; benzaldehyde, 2·98, 3·15; aniline, 1·38, 1·48; amyl acetate, 4·65, 5·14; ethylene bromide, 2·27, 2·81; *iso*amyl alcohol, 1·91, 2·47; chloroform, 3·71, 5·60.

A. A. E.

**Partition of a Substance between two Solvents and the Solution Field of Force.** N. A. SCHILOV and L. K. LEPIN [with M. P. JANTSCHAK] (*Nachr. Phys.-Chem. Lomonossow-Ges.*, 1920, **1**, 1—103; from *Chem. Zentr.*, 1922, iii, 541—542).—The partition of a dissolved substance between two liquid phases changes with varying concentrations and only remains constant in particular cases owing to the operation of compensating factors. The partition does not in general depend on the solubilities in the individual solvents; this relationship, in fact, only holds at the triple point of the three phases. The isotherms for the changes in concentration are different for each phase and are not linear. The relation $k=c_1^2/c_2$ is only a particular case of the relation $k=c_1^m/c_2=q\,.\,c^1/c_2^n$, where $n$ is an integer or fraction and given by $n=\log \beta_1/\log \beta_2$, $\beta_1$ and $\beta_2$ being factors expressing the changes in the solution field of force (lösungskraftfeld) depending on concentration. The partition coefficient thus obtained is constant for many systems, excepting those where the two solvents have a considerable reciprocal solubility, and where chemical factors may play a part.

G. W. R.

**Solubility of Liquids in Liquids. The Partition of the Lower Acids, particularly Formic, between Water and various Organic Solvents.** NEIL E. GORDON and E. EMMET REID (*J. Physical Chem.*, 1922, **26**, 773—789).—The partition

ratios at 25° of formic acid between water and the following respective solvents: cotton-seed oil, petroleum, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide, and bromoform have been determined. In like manner, the respective partitien ratios at 25° of acetic acid between water and either cotton-seed oil or petroleum, of propionic and butyric acids between water and cotton-seed oil have been determined. The results have been employed to determine the so-called solubilities of the acids in the solvents and vice versa. J. S. G. T.

**The Behaviour of Two Metals towards One Another when Dissolved in Mercury.** G. TAMMANN and W. JANDER (*Z. anorg. Chem.*, 1922, **124**, 105—122).—The authors investigated the affinity of one metal for another when dissolved in mercury: (1) by measuring the freezing-point depression of the compound crystals and comparing this with that of the components, (2) by measuring the influence of the one metal on the *E.M.F.* concentration-curve of the other dissolved in a third more noble liquid metal. Thus the addition of small amounts of a more noble to a less noble metal has but a very small effect on the *E.M.F.* if the compound of the two metals is very highly dissociated, whereas, if a stable compound is formed, then a sudden change in the *E.M.F.* is caused when the concentrations of the metals correspond with the composition of this compound. The following intermetallic compounds were found to be very stable: AuZn, $Mg_2Sn$, $CeSn_2$, and $Ce_4Bi_3$, having very high affinity constants. AuZn $K=3{\cdot}4\times10^7$. $Mg_2Sn$ $K=1\times10^{10}$. $CeSn_2$ $K=1\times10^{40}$. $Ce_4Bi_3$ $K=3\times10^{120}$. Cf. water $K=4{\cdot}6\times10^{78}$. Others were very highly dissociated in solution in mercury; for example, compounds of gold with cadmium and lead, of silver with zinc and cadmium, of copper with zinc and cadmium. W. T.

**Systems in which Metals Crystallise.** JOHN L. HAUGHTON and G. WINIFRED FORD (*Trans. Faraday Soc.*, 1922, **18**, 112—118).—Of the twenty-nine elements the crystalline structures of which have been determined by *X*-ray analysis, five only are exceptions to the rule that all elements of the same periodic series crystallise in the same system. In nearly every case, alloys which form a homogeneous series of solid solutions right across the equilibrium diagram, crystallise in the same system. There appears to be no relationship between the changes which occur in the physical properties of metals at the melting point and the crystalline habit of the metals. A possible exception occurs in the case of the electrical resistivity of the metals in the odd series of group 5. J. S. G. T.

**Solutions, Suspensions, Colloids.** N. P. PESKOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 73—99).—The theoretical considerations developed by the author lead to the following conclusions. The modern doctrine of colloids deals with a conception of heterogeneity which is totally different from that assumed by the doctrine of phases, but is identioal with the molecular–kinetic view of the universe; the latter is termed the generalised conception

of heterogeneity. The notion of dispersion current in the chemistry of colloids must be regarded as composed of two different conceptions, distinguished as qualitative and quantitative dispersion. The former of these is synonymous with the generalised conception of heterogeneity referred to above, and has no special bearing on systems represented by suspensions, colloids, and solutions. The latter, possessing a dimensional character, differs from the idea of a phase only in that the latter is characterised by the spacial magnitudes of its separate elements. Thus all systems to which the term quantitative is applied must be considered to be polyphasic.

Physical theories of colloids in general postulate that: (1) suspensions, colloids, and true solutions are systems, the qualitative differences between which may be regarded as functions of their degrees of dispersion, (2) colloids represent typical polyphase systems, and (3) all the characteristic properties of colloids are merely the results of the magnitudes of the molecules. The logical objection to such theories is that they accept as results of the doctrine of dispersion the hypothetical assumptions on which this doctrine is based.

The author considers that only careful investigation, from all points of view, of the process of coagulation and of the adsorption phenomena accompanying them will decide the question of the heterogeneity of colloids in their normal condition. T. H. P.

**Electrical Colloid Synthesis.** SVEN BODFORSS and PER FRÖLICH (*Koll. Chem. Beihefte*, 1922, **16**, 301—340).—Svedberg's method of synthesis of colloids has been investigated for the case where the induction coil current is replaced by a high tension symmetrical alternating current and the dependence of the amount of dispersion on the dimensions of the oscillation circuit determined. The dispersion of copper, tin, lead, zinc, antimony, aluminium, silver, magnesium, bismuth, and thallium by Svedberg's method and the present method has been compared, and it is shown that for the more easily dispersed metals the present method is inferior to the original Svedberg method, the yield being about one-half to two-thirds that obtained by the older method. In the case of the harder metals, the dispersion is about the same by both methods. Alloys belonging to the systems lead–tin and antimony–zinc have been dispersed by the present method and the sols produced examined. J. F. S.

**Winkelblech's Phenomenon or Pseudo-extraction and its Importance in Colloidal Chemistry. New Methods of Extracting Solids.** K. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 96—107).—Winkelblech (A., 1907, ii, 17) found that when certain pseudo-solutions are treated with various non-aqueous solvents insoluble in water, the solid disperse phase passes partly or completely into the liquid, non-aqueous phase, throughout which it becomes distributed in the form of a gel. This phenomenon is usually regarded as a special case of adsorption, but the results obtained on examining different combinations of disperse phases and non-aqueous solvents are completely incompatible

with this view. The effect seems to be due rather to mechanical seizure of the molecules of the solid phase by disintegrated liquid drops of lower specific gravity or to attraction of these molecules *to the bottom by molecules of a heavier liquid.*

From a pseudo-solution of gelatin part of the sol may be drawn to either the surface or the bottom of the liquid by treatment with light petroleum, chloroform, carbon disulphide, etc., and owing to the resemblance of the phenomenon to extraction the author terms it "pseudo-extraction."

For the velocity of transport of the molecules, Lewis's formula, $V=2r^2S(S-S_1)/9\eta$, should be valid, $S$ and $S_1$ being the specific gravities of the solid and liquid phases, $r$ the radius of the molecules, and $\eta$ the coefficient of viscosity, but greater exactitude would be attained by addition of the term, $2r^2S(S-d)/9\eta$, $d$ denoting the specific gravity of air.

The fact that sols of silicic acid, Prussian blue, and almost all metals remain unchanged when treated with light petroleum, benzene, and similar liquids is explained on the assumption that, for certain values of $S$ and $S_1$ the magnitude of $V$ will be negative, the specifically lighter molecules of air and light petroleum being then not in a condition to draw upwards the heavier molecules of the sols of metals and various oxides.

The results of experiments on the pseudo-extraction of gelatin, agar-agar, and sodium oleate show that the quantity of the colloidal substance thus extracted is not proportional to the concentration; when the latter is very high, no pseudo-extraction takes place. For every disperse phase, the phenomenon appears to exhibit an optimum concentration and an optimum temperature. In no case, however, is it possible to remove by pseudo-extraction the whole amount of a sol occurring in the disperse phase. The excess above the normal proportion of potassium hydrogen tartrate or sodium sulphate present in supersaturated solution is withdrawn *instantaneously from the latter by shaking with light petroleum.* The same occurs when an aqueous alcoholic solution of sucrose is similarly treated, but in this instance the sucrose withdrawn partly redissolves in the aqueous alcoholic layer on prolonged keeping of the system after being shaken with the light petroleum. T. H. P.

**General Method for Obtaining Gels of Inorganic Salts, and its Relation to Theories of the Colloidal State.** K. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 91—96).—Treatment of a solution of sodium (potassium, etc.) naphthenate in a hydrocarbon containing excess of naphthenic acid with hydrogen chloride or carbon dioxide yields colloidal sodium chloride or carbonate. With heavy metal salts of naphthenic acid, which dissolve readily in benzene, toluene, or light petroleum, excess of naphthenic acid is not required; colloidal cupric and mercuric chlorides, etc., are obtainable in this way. The naphthenic acid may be replaced by oleic acid. The products formed show Brownian movement and the corresponding ultramicroscopic appearance. The sol first formed rapidly undergoes coagulation

but not throughout its entire mass, part remaining in a condition of pseudo-solution detectable ultramicroscopically.

Treatment of ferrous sulphate in the above way results in the formation of a white precipitate which, as oxidation proceeds, is gradually converted first into a black sol of triferric tetroxide and ultimately into a brown sol of ferric oxide. The action of hydrogen chloride on ferric naphthenate yields, not ferric, but ferrous chloride, the hydrogen chloride acting as a reducing agent under these conditions.

These and allied phenomena do not appear to be explicable by any of the existing theories of the colloidal state, or by von Weimarn's crystallisation theory, which is generally accepted. Neither this author's formula for expressing the course of separation of precipitates, nor that given by Nernst to indicate the velocity with which a precipitate forms round centres of crystallisation, takes into account the attraction or affinity between solvent and solute, which constitutes an important factor; in many cases, the whole process of crystallisation is the resultant of the force uniting the molecules and the affinity of the latter for the solvent.

The author regards gels and sols as the extreme and final stages of the interactions between solid and liquid phases, intermediate stages being represented by crystals of various degrees of symmetry.

T. H. P.

**Sensitisation of Coagulation Processes: Colloids as Indicators of Photo-electric Effects.** N. P. Peskov (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 101—104).—Anthracene is found to exert a sensitising action on the coagulation of sols of arsenic trisulphide, platinum, and carbon, but it is not known if this action is exercised towards all sols or if it is limited to those carrying a definite charge. The action does not depend on chemical transformation of the anthracene or on its fluorescence, but lies in the electronic transpositions taking place in the system under the influence of insolation. Hence colloids constitute a new type of indicator for photo-electric effects. Reference is made to the various possible interpretations of the mechanism of the coagulation of colloids under the sensitising action of anthracene.

T. H. P.

**Flocculation by Mixtures of Electrolytes.** H. Freundlich and P. Scholz (*Koll. Chem. Beihefte*, 1922, **16**, 267—284).—The authors have confirmed the results of Odén, to the effect that the coagulating properties of a salt are diminished or destroyed by the presence of a second salt, but in contradiction to Odén they have also found that the reduction is not due to a diminution of the kation action by the anion but rather to an antagonism between the kations. The antagonistic action is measured by mixing Odén's sulphur sol with a quantity of an electrolyte insufficient to cause flocculation and then determining the quantity of a second electrolyte necessary to effect this change. In the case of ion pairs with strong antagonism such as magnesium–lithium, or magnesium–hydrogen, the coagulation value of the magnesium

is a whole number multiple of the value obtained when the coagulation is effected by magnesium alone. The anions have also an influence in the diminution of the coagulation value in the order citrate''' > sulphate'' > chloride'. Definitely hydrophobic sols, such as Weimarn's sulphur sol and Donau's gold sol, do not exhibit the above-named phenomena. In these cases the coagulation values of sols containing electrolytes are always less than those of the pure sols; that is, the action of the two electrolytes is additive, as is to be anticipated from the coagulation hypothesis of hydrophobic sols. In these cases also, the coagulum cannot be peptised by electrolytes. The behaviour of Odén's sulphur sol is probably to be connected with its distinct hydrophilic character; that is, with the hydration of the micellæ. In the case of arsenic sulphide sol, a certain antagonism is observed for salts such as lithium chloride and magnesium chloride. J. F. S.

**Coagulation of Manganese Dioxide Sol by Different Electrolytes.** PHANI BHUSAN GANGULY and N. R. DHAR (*J. Physical Chem.*, 1922, **26**, 701—714).—The coagulative powers of different electrolytes on manganese dioxide sol do not follow the Schulze-Hardy law, namely, the higher the valency of an ion the greater its precipitating action on a colloid. Changes of concentration of the sol alter the relative order of the electrolytes when arranged according to their coagulative powers. Coagulative power is not purely a function of valency, but is more a specific property of the ions, and is influenced, among other factors, by the time allowed for coagulation and the presence of anions.

J. S. G. T.

**Rôle of the Hydrogen-ion Concentration in the Precipitation of Colloids.** HERMANN V. TARTAR and ZALIA JENCKS GAILEY (*J. Amer. Chem. Soc.*, 1922, **44**, 2212—2218).—The effect of the hydrogen-ion concentration on the precipitation of mastic and gamboge sols by solutions of acids and salts has been investigated. It is shown that acids cause precipitation at the same hydrogen-ion concentration irrespective of the concentration of the colloid. The negative ion of the acid is without effect. Various potassium and ammonium salts precipitate the sols at the same concentration provided that the hydrogen-ion concentration is kept approximately constant. The precipitating values of the salts vary directly as the concentration of the colloid at the same hydrogen-ion concentration. The stabilising or peptising effect of the ion bearing a charge similar to that of the colloidal particle is shown to be very limited if it exists at all. J. F. S.

**Soaps and Proteins. II. Colloid Chemistry of Soap Manufacture, Analogies in the Colloid Chemistry of Soaps, Albumins, and Tissues. III. Colloid Chemical Behaviour of Fatty Acids and their Derivatives and the Analogous Behaviour of Neutral Proteins and their Derivatives.** MARTIN H. FISCHER [with GEORGE D. MCLAUGHLIN and MARIAN O. HOOKER] (*Koll. Chem. Beihefte*, 1922, **16**, 99—179; cf. this vol., ii, 430).—A continuation of previous work. The principles of the hot and

cold processes in the soap industry are described. The significance of some of the constants of oils and fats, such as the density saponification number, the iodine number, and the Reichert-Meiss number, is pointed out. The physical properties of soaps are discussed. An account of experiments on the systems, globulin-water, globulin-sodium hydroxide, globulin-acid, globulin-metallic chloride, gelatin-water, gelatin-alkali hydroxide, gelatin-acid, and gelatin-salt is given and peptisation and coagulation are discussed The theory of poisoning by ammonium and heavy metal salts is discussed and it is shown that these substances combine with the protoplasm with the formation of compounds which are much less hydrated than the normal protoplasm compounds, and that this constitutes the poisoning. Reproductions of a large number of photographs, illustrating the experiments, are contained in an appendix to the paper. J. F. S.

**Action of Anions, particularly the Hydroxyl-ion, on the Colloidal Condition of Night-blue.** S. AKAMATSU (*Kolloid Z.* 1922, **31**, 209—215).—The effect of various anions on the surface tension of solutions of night-blue has been investigated to ascertain whether or no the position of the hydroxyl-ion in the activity series found by Traube (A., 1912, ii, 740) is correct. This series places the hydroxyl ion after the halogen ions instead of in the most active position as was expected. The surface tension of 0·2% solutions of night-blue containing concentrations varying from $N/10$ to $N/1000000$ of potassium iodide, bromide, chloride, nitrate, thiocyanate, chlorate, sulphate, hydroxide, and dihydrogen phosphate has been measured. It is shown that the addition of the various electrolytes causes the surface tension to rise to a maximum and then to fall to a value approaching the water value with decreasing concentration of the added electrolyte. The measurements showed that the hydroxyl ion is the most active of all anions and that the reason for the position given to it by Traube lies in the fact that he took as his concentration of hydroxyl ions the concentration of the hydroxide added. In the present work the concentration of the hydroxyl ion has been measured *electrometrically*. J. F. S.

**The Equilibrium between some Organic Substances.** H. HAMMERSTEN (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 16, 1—14).—The equilibrinm constant, $K$, for the reaction between phenylhydrazine and acetone or acetaldehyde has been investigated by the solubility method of Euler and Svanberg (A., 1921, i, 68), and also by the measurement of the refractive indices of the solutions. The various results are not very consistent, but in the case of acetone–phenylhydrazine the value of $K$ appears to be about $7—9 \times 10^{-4}$, and in the case of acetaldehyde–phenylhydrazine about $10^{-3}$. W. O. K.

**The Solubility of Calcium Carbonate in Water in Equilibrium with a Gaseous Phase containing Carbon Dioxide.** YUKICHI OSAKA (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 131—141).—The solubility of calcium carbonate in water has been calculated

from the data given by McCoy and Smith (A., 1911, ii, 379). It is assumed that carbon dioxide dissolved in water is a much stronger acid than acetic acid (cf. Strohecker, A., 1916, ii, 522, and Pusch, A., 1916, ii, 477, 557) and that the gas is only slightly combined with water. The apparent first dissociation constant and the second dissociation constant of water are taken as $3 \cdot 50 \times 10^{-7}$, and $4 \cdot 91 \times 10^{-11}$, respectively, and the solubility product of calcium carbonate (calcite) at 25° was calculated to be $7 \cdot 24 \times 10^{-9}$. The solubility of calcium carbonate in water, in the presence of carbon dioxide, is given by $C = [Ca^{\cdot\cdot}] + 1 - \gamma/2\gamma[HCO_3']$, where $\gamma$ is the degree of dissociation of calcium hydrogen carbonate, assuming that the solution is ionised to the same extent as that of calcium acetate of the same concentration. Formulæ are given for the relationship between $[Ca^{\cdot\cdot}]$, and $[HCO_3']$, and the partial pressure of carbon dioxide. W. E. G.

**The Propagation of Explosion Waves in Gases contained in Tubes of Varying Cross-section.** COLIN CAMPBELL (T., 1922, **121**, 2483—2498).

**Limits for the Propagation of Flame in Vapour-Air Mixtures. II. Mixtures of More than One Vapour and Air at the Ordinary Temperature and Pressure.** ALBERT GREVILLE WHITE (T., 1922, **121**, 2561—2577).

**The Velocity of the Action of Oxygen, Hydrogen Sulphide, and the Halogens on Metals.** G. TAMMANN and W. KÖSTER (*Z. anorg. Chem.*, 1922, **123**, 196—224).—When iodine, chlorine, or air acts on a metal, a variety of surface colours is formed, and these colours give the rate of thickening of the film of compound formed (cf. A., 1920, ii, 248). The rate of chemical action is high hut diffusion of the gas through the film of compound is slow. In the case of iodine, the rate is inversely proportional to the thickness of the film and is independent of the temperature. There is in the case of the action of iodine on silver a change in the velocity at 145° which is the transition temperature of silver iodide. In the case of the action of moist air containing chlorine and bromine on copper, silver, and lead there is a parabolic relationship between the time of action and the thickness of film. The same holds in the case of the oxidation of metals. At high temperatures oxidisable metals are almost immediately covered with a thin film of oxide which protects the metals.

Hydrogen sulphide reacts rapidly with copper and manganese, more slowly with silver, and still more slowly with lead. Iron, cobalt, nickel, chromium, antimony, bismuth, tin, aluminium, zinc, and cadmium show no change after several days' contact with the gas. The action of air on copper-zinc alloys was also investigated. W. T.

**The Formation of Oxides of Multivalent Metals from their Hydroxides.** HANS VON EULER and ULF VON EULER (*Z. anorg. Chem.*, 1922, **124**, 70—80).—The temperature-coefficient of the coagulation of albumin is very high, the rate being doubled

for an increase of temperature of 2°. The rate of dehydratio of copper hydroxide was measured at different temperatures. Th temperature-coefficient was very high, as in the coagulation c albumin, but was found to decrease with increasing temperatur 40—45°=3·0 for 5°, 55—60°=1·8. The results were not i agreement with Arrhenius's formula (A., 1889, 1103), which le the authors to the conclusion that the dehydration consists c several reactions. The rate of dehydration was measured color metrically. The isoelectric points for copper hydroxide is $3\times10^{-1}$ as obtained from the equation $I=\sqrt{K_s.K_w/K_b}$. W. T.

**Velocity of Hydrolysis of Ethyl Acetate.** HERBERT S HARNED and ROBERT PFANSTIEL (*J. Amer. Chem. Soc.*, 1922, **44** 2193—2220).—The unimolecular velocity constants of the hydro lysis of ethyl acetate in the presence of hydrochloric acid of man concentrations bave been accurately determined at 25°. A solutio of the general equation for the velocity of hydrolysis has bee obtained and the velocity constants have been calculated by th general equation. In four series of measurements, it has bee found that the curve of the velocity constants divided by th molecular concentration of hydrochloric acid against log $c_1$, wher $c_1$ is the molecular concentration of hydrochloric acid, shows a minimum at 0·07—0·08*N*-acid. This is similar to the curve o the individual hydrogen-ion activity coefficient against log $c_1$ which has a minimum at 0·15—0·18*N*-acid. It has been show that the velocity constant divided by the product of the activitie of the hydrogen ion and the water molecule is not a constan at different acid concentrations but has a maximum at 0·3*N* hydrochloric acid. Some factors which may cause this deviatio from constancy have been suggested. The kinetics of the hydro lysis of ethyl acetate are very complex, but the authors are of th opinion that the evidence obtained in the present work shows tha the method employed is in general the correct method of attackin this problem. J. F. S.

**Velocity of Inversion of Sucrose as a Function of th Thermodynamic Concentration of the Hydrogen-ion** HAROLD A. FALES and JACQUE C. MORRELL (*J. Amer. Chem. Soc.* 1922, **44**, 2071—2091).—The velocity of hydrolysis of sucrose b solutions of sodium hydroxide, acetic acid, and hydrochloric aci of various concentrations has been determined at 35° and th thermodynamic hydrogen-ion concentration has been calculate from *E.M.F.* determinations of the reaction mixtures at the sam temperature. It is shown that the addition of sucrose to solution of hydrochloric acid causes a definite increase in the thermo dynamic concentration of hydrogen-ion over the whole range o concentration of the acid. In the case of acetic acid, a maximun increase in hydrogen-ion concentration is observed which diminishe as the concentration of hydrogen-ion decreases, on the additio of sucrose. The addition of sucrose to sodium hydroxide appear to cause an increase in the thermodynamic concentration o

hydrogen-ion. The thermodynamic concentration of hydrogen-ion in the system remains appreciably constant during the course of the inversion process. The velocity of inversion of sucrose by hydrochloric acid is proportional to the thermodynamic concentration of hydrogen-ion only for the limited range of concentration of acid which lies between 0·01*N* and 0·001*N*. The bimolecular velocity constants, reduced to unit thermodynamic hydrogen-ion concentration, are constant with changing concentrations of sucrose only for each molecular concentration of hydrochloric acid between 0·01*N* and 0·3*N*. These constants vary considerably for different concentrations of acid. Evidence is adduced which shows that for acetic acid, the undissociated molecule is not a positive catalyst in the inversion process; or that there are other factors entering here which have never been considered. With strong acids, the inversion process does not appear to be strictly unimolecular, especially in the early periods of the reaction. Within the limits of the concentrations of the reactants used, no appreciable change in volume was noticed when the solutions of hydrochloric acid and sucrose were mixed. J. F. S.

**Generator Gas Equilibrium at High Pressures.** KARL JELLINEK and ALOIS DIETHELM (*Z. anorg. Chem.*, 1922, **124**, 203—229).—The electric furnace employed was a modification of that used by Nernst (*Z. Elektrochem.*, 1907, **13**, 52); it allowed measurements to be carried out at 1300° and at 150 atmospheres. The reaction $C+CO_2 \rightleftharpoons 2CO$ was investigated between 800° and 1000° at pressures up to 50 atmospheres. Various forms of charcoal were employed, and the equilibrium, which was well defined, was practically the same in each case, and again the same in the case of graphite. The law of mass action was obeyed at all pressures. The integration constant of the reaction isochore of generator gas equilibrium was found to be 3·876; this agrees well with the value calculated by means of Nernst's heat theorem (3·80). The authors show that the maximum work of this reaction is equal to the heat effect if the reaction is carried out isothermally and reversibly and *if the excess of oxygen has the same pressure as the carbon dioxide* formed. W. T.

**Catalytic Activity of Copper.** O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, **26**, 715—727).—In continuation of previous work (this vol., i, 445), the authors have investigated the catalytic reduction of nitrobenzene to aniline by hydrogen in the presence of copper catalysts prepared by the reduction of the precipitated oxide. Sabatier's conclusion that a catalyst so prepared is more efficient than one prepared from an ignited nitrate was confirmed. By the use of the former catalyst, much lower rates of supply of hydrogen may be used without reduction in yield, and the reaction may be carried out at a much greater rate. The best temperature for carrying out the reduction was found to be about 260°. A small amount of iron in a copper catalyst prepared from an ignited oxide prevents the rapid decrease in activity of the

catalyst. Copper deposited on asbestos was found to be capable of effecting the reduction at a much greater rate per gram of copper than copper alone, but with high rates of supply of nitrobenzene, it quickly lost its activity. Copper on asbestos is a better catalyst than an equal volume of copper on pumice. J. S. G. T.

**Selective Activation of Alumina for Decarboxylation or for Dehydration.** HOMER ADKINS (*J. Amer. Chem. Soc.*, 1922, **44**, 2175—2186).—Alumina has been preferentially activated for decarboxylation or for dehydration by modifying the method of preparation. This has been accomplished by obtaining aluminium hydroxide and hydrated alumina by precipitation from its salts or esters in water or xylene solution, and by preparing it by the action of water vapour on aluminium alkyl oxides, both in the pure state and when the latter are impregnated in pumice. The extent to which selective activation has been accomplished is indicated by the following figures, which give the relative " ethylene efficiency " of the variously prepared catalysts with ethyl acetate vapour at 465° : 34, 38, 41, 50, 107, and 150. The catalysts indicated were prepared as follows : by melting aluminium *iso*propoxide on pumice and exposing to moist air for eighteen hours (34); as last, but aluminium *iso*butoxide was used (38); by the action of moist air on aluminium methoxide; this was used as compressed tablets and contained traces of mercury (41); alumina from aluminium butoxide supported on pumice as above (50); tablets made from the precipitate produced by the action of hydrochloric acid on solutions of sodium aluminate (107); and tablets made from alumina obtained by the action of water on aluminium amalgam (150). An hypothesis has been advanced in which it is considered that the catalytic activity of alumina is conditioned by its molecular porosity, or the distances between the aluminium atoms and this, in part, is determined by the size, shape, and position of the radicles attached to the aluminium when the aluminium compound passes into the solid state. All the experimental evidence obtained with alumina catalysts is in complete harmony with this hypothesis. In terms of this hypothesis, it is held that decarboxylation is favoured by large pores in the alumina and that ethylene formation is favoured by small pores, large and small referring to units of molecular dimensions. The work of Milligan and Mead (this vol., ii, 447) on the dehydration and *X*-ray pattern of aluminium hydroxide is discussed in its relation to catalytically active alumina. The results obtained by Palmer (A., 1921, ii, 542), in the use of electrolytic copper and copper by reduction for the hydrogenation of alcohol, are explained on the basis of the hypothesis noted above. Cf. Langmuir (this vol., ii, 629). J. F. S.

**The Influencing of Catalysts and Specifically Active Catalysts.** KARL W. ROSENMUND and F. ZETZSCHE (*Ber.*, 1922, **55**, [*B*], 2774).—A reply to Abel (cf. Rosenmund and Zetzsche, A., 1921, ii, 320, 392, 393; this vol., ii, 41; Abel, A., 1921, ii, 542; this vol., ii, 26). H. W.

**Kinetics of Inductive Processes: Schönbein's Reaction.** A. V. Pamfilov and N. N. Petin (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1922, **6**, 221—231).—The authors discuss previous work published on the influence of ferrous oxide on the liberation of iodine from an iodide by the action of hydrogen peroxide, and give the results of their own experiments on this reaction. It is found that not only the velocity of the initial stage of the reaction, but also the nature of its dependence on the concentration of the iron salt and on the corresponding acidity are completely different according as the iron is in the ferric or the ferrous condition. The liberation of iodine by ferric oxide or hydrogen peroxide separately is considerably accelerated when the two reactions occur together, and the velocities of the separate, and that of the combined, reactions *increase with increase of the concentrations of all the components*; the acidity of the medium is of comparatively little influence, but in general accelerates the reaction.

On the other hand, in neutral and faintly acid media the reaction is accelerated more by ferrous oxide than by ferric oxide in low concentration, but for definite conditions of concentration the *reaction is retarded by increasing the concentration of the ferrous* oxide either absolutely or in relation to the potassium iodide; this retardation is observed also in an acid medium. Increase in the acidity also retards the reaction considerably. This phenomenon disappears when the concentration of the potassium iodide increases and the solution is rendered strongly acid, especially as liberation of iodine by the acid becomes pronounced under these conditions.

Hence the diminution in the sensitiveness of Schönbein's reaction in a neutral medium caused by increase in the concentration of the catalyst (cf. Meissner, "Untersuchungen über den Sauerstoff," 1868, 78—80; Struve, *Z. anal. Chem.*, 1869, **8**, 319) is not fortuitous but holds generally, both in acid and in neutral solutions. The results of replacement of the acid by the corresponding concentration of a sulphate show, as was found by Brode (A., 1901, ii, 443) for ferric-ions, that the influence of increased acidity is not to be referred to diminished concentration of the ferrous ions and that *the hydrogen-ions must here play a part.*

The mechanism of the action of ferrous oxide, typical of inductors in general, is probably based on its spontaneous oxidation, and the retarding influence exerted on the reaction by acidity is related to the great stability of ferrous-ions in an acid solution. T. H. P.

**Union of Hydrogen with Acetylene Derivatives. XV. Velocities of Catalytic Reactions.** J. S. Zalkind (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 199—211).—The author discusses the results obtained by various investigators on the course followed by reactions occurring under the influence of enzymes and other catalysts. The general conclusion drawn is that, even when catalysts so chemically simple as palladium and platinum are used, the course of the reaction is often quite complex, and that no essential difference exists between the actions of these simple catalysts and those of enzymes. In both cases, it is necessary to

assume the formation of intermediate compounds between the catalyst and the reacting compounds, although with regard to the means by which such intermediate compounds are formed—whether by chemical reaction or by simple adsorption—opinions differ. Adsorption phenomena may, indeed, exhibit complex character and a sharp distinction between adsorptive and chemical phenomena is scarcely possible. T. H. P.

**Speculations concerning the Positive Electron.** [SIR] OLIVER LODGE (*Nature*, 1922, **110**, 696—697).—According to Larmor's theory, the positive and negative electrons can only differ in one being the mirror-image of the other. No positive electron in this sense has yet been discovered. Both positive and negative electrons are supposed to be extremely mobile, and the forces between them immense, so that they instantly bind themselves together into a compact and stable structure consisting of several thousands of each kind, the simplest and lightest of these composite structures being the hydrogen nucleus or proton. The proton for the first time allows a negative electron to revolve round it without being absorbed into its composition. On the mirror-image hypothesis, however, it becomes difficult to explain why only negative electrons should occur in the satellite systems; that is, why some atoms should not have nuclei with a surplus of negative charge, and be attended by positive electrons. The case of a number of primary electrons, both positive and negative, is considered. If, in the many possible ways of structural packing, something less than half the atomic nuclei formed were of the kind with positive satellites, whilst the other approximate half were of the negative satellite variety, the two classes would speedily combine with great violence and thereby form the tight-packed and stable nuclei of heavier atoms, until the complexity was too great to ensure stability. The combination of nuclei would cease only when they were protected by a screen of similar electrons, of which the sign might be positive or negative, but could not be both; that is, the resulting atoms could not be of opposite varieties. Thus the outlying satellites are all of one sign, either in every case or in so vast a preponderance of cases that no exceptions are as yet manifest. The free lifetime of the less plentiful variety would be too brief for ordinary detection, but it is suggested that by means of the shattering of nuclei and rapid methods of detection, the composite nature of the proton may possibly be demonstrated by the emission of something fractional of extreme instability. In this connexion, attention is directed to the fact that the atomic bombardment of aluminium yields particles of specially long range. A. A. E.

**Motions of Electrons in Argon and Hydrogen.** J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **44**, 1033—1052; cf. this vol., ii, 277, 494).—Further measurements have been made of the movement of electrons in argon and hydrogen, and in mixtures of the two gases, in a uniform electric field. The velocity of the electrons ($W$) in the direction of the electric force, their mean velocities of agitation in the gas ($u$), their mean free path ($l$), the

loss of energy on collision with a gas molecule (λ), and the factor (*k*) by which the energy of agitation of an electron exceeds the energy of a molecule of gas at 15°, are given for varying values of $Z/p$, where $Z$ is the fall in potential in volts, and $p$ is the gas pressure in millimetres. The loss in energy of an electron on collision with a molecule of argon is extremely small. When moving with a velocity of agitation of $12{\cdot}6\times10^7$ cm. per sec., the fraction of energy lost by an electron on collision with a molecule is $1{\cdot}6\times10^{-5}$ in argon, $5\times10^{-3}$ in nitrogen, and $4\times10^{-2}$ in hydrogen, and the corresponding mean free paths are 0·147 cm. in argon, 0·029 cm. in nitrogen, and 0·035 cm. in hydrogen, the gases being at 1 mm. pressure.

In the case of argon, whereas $W$ increases steadily with increase in $Z/p$, $u$ increases to the constant value, $20{\cdot}7\times10^7$ cm. per sec. Between the values of $Z/p$, 1·25—15, the velocity of agitation remains practically constant, whilst the loss of energy on collision steadily increases. This is due to a large loss in energy in collisions with velocities greater than the mean. The free path of an electron in argon at 1 mm. pressure has a maximum value of 1·6 cm. for the velocity $3{\cdot}75\times10^7$ cm. per second, whereas the mean free paths of nitrogen and hydrogen show minima in the neighbourhood of $8\times10^7$ cm. sec. The large increases in the mean free paths of the electrons as the velocity diminishes are very striking.

The addition of argon to hydrogen, whilst reducing $W$, the velocity in the direction of the electric force, scarcely affects $u$, the mean velocity of agitation of the electrons. This is in agreement with the small loss in energy on collision with a molecule of argon. The mean free paths in argon, for velocities of agitation less than $11{\cdot}5\times10^7$ cm. per second, were found by measurement of the mean free paths in mixtures of hydrogen and argon. W. E. G.

**The Motion of Electrons in Carbon Dioxide.** M. F. SKINKER (*Phil. Mag.*, 1922, [vi], **44**, 994—999).—The apparatus used was similar to that of Townsend and Bailey (cf. this vol., ii, 277, 494). Curves are given comparing the speed of electrons in carbon dioxide, nitrogen, and hydrogen. Values for the mean free path of the electron, its speed in the direction of the electric force, its velocity of agitation, and the proportion of energy lost on collision with a molecule of gas, are tabulated against different values of $Z/p$ (cf. Townsend and Bailey, preceding abstract). A sudden increase in the loss of energy which occurs on collision between an electron and a molecule of carbon dioxide is observed between the velocities of agitation $13\times10^7$ and $15\times10^7$ cm. per second. W. E. G.

**The Constitution of the Chemical Elements.** FRIEDRICH WÄCHTER (*Z. anorg. Chem.*, 1922, **123**, 1—13).—A theoretical paper. The author assumes that the light ether is a ponderable gas, an atom of which has a mass 1/1800 the mass of an atom of hydrogen. He regards the elements as different condensation forms of the light ether, the number of ether atoms in an atom of any element being 1800 times the atomic weight of the element. This is applied to the atomic heat of elements and to the spectral lines. W. T.

**The Disintegration of Chemical Elements.** FRIEDRICH WÄCHTER (*Z. anorg. Chem.*, 1922, **123**, 14—30).—A theoretical paper. The author assumes that hydrogen and helium atoms are made up of light ether atoms, and that other elements are built up of hydrogen and helium atoms. He then endeavours to explain the disintegration of the radio elements. W. T.

**Electronic Structures of Atoms.** MAURICE L. HUGGINS (*J. Physical Chem.*, 1922, **26**, 601—625).—A theoretical paper in which the Lewis hypothesis of valency and atomic structure is assumed to be correct for the lighter atoms. The evidence in favour of a tetrahedron of electron pairs, rather than a cube of single electrons, being the most stable arrangement for the valency shell of these atoms, is put forward. It is shown how the stability of such an arrangement may be the result of the deviation of the force law between two electrons from Coulomb's law at small distances. The chief requirement for this purpose is that as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 Å., the force then decreasing, for a considerable proportion of the remaining distance at least. As a result of a law of this type, whenever two electrons, forming part of an atomic shell, are forced close enough together, they come still closer to each other that is, the pair off, and similarly from three pairs aided by the attraction of an atomic nucleus and the repulsion of other electrons, triplets are formed. Based on this assumption and on the idea that the electrons in an atomic shell tend to place themselves opposite the centres of the faces of the imaginary polyhedron formed by the electron groups in the next underlying kernel shell, an arrangement of electrons is obtained for each element in each valency stage, with a few exceptions which have not yet been deduced. These arrangements conform with the known properties of the elements, and account for the periodic relationships in a simple and logical manner. J. F. S.

**Bohr's Model of the Hydrogen Molecules and their Magnetic Susceptibility.** KÔTARÔ HONDA (*Nature*, 1922, **110**, 664—665).—Since, according to Langevin, hydrogen molecules should have a paramagnetic susceptibility, it has hitherto been assumed that Bohr's model does not explain the diamagnetic property of the gas. The actual diamagnetic susceptibility, as determined by Soné, is shown to lie between the two values calculated when the validity of Bohr's model is assumed in the case of $n+n'=1$ and $n+n'=2$, where $n$ and $n'$ are the azimuth and radial quantum numbers. A. A. E.

**The Normal Helium Atom and the Quantum Theory.** J. H. VAN VLECK (*Phil. Mag.*, 1922, [vi], **44**, 842—869).—A study is made of the Kemble model of the helium atom. In this model the two electrons are arranged with axial symmetry. The energy of this atom has been computed, and the calculation has given a value of 20·7 volts for the ionisation potential, instead of 25·4

demanded by experiment, the discrepancy being slightly greater than for the Bohr model. It does not seem possible to devise a satisfactory symmetrical model of helium based on the conventional quantum theory of atomic structure. W. E. G.

**The Neuburger Nuclear Model.** MAXIMILLIAN CAMILLO NEUBURGER (*Physikal Z.*, 1922, **23**, 389).—A reply to Meitner (cf. this vol., ii, 702). The author's model of the structure of the atomic nucleus is not dependent on the existence of *iso*helium in the free state. The nuclear formula requires, however, that groups, *composed of three hydrogen nuclei and an electron, shall be capable* of existence in the nucleus itself. W. E. G.

**Negative Valency and Co-ordination Number.** E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 281—290).—The most pronounced negative affinity is accompanied by non-metallic properties, so that, if it is assumed that negative affinity is the result of a tendency of the rings of valency electrons to attain saturation, it becomes necessary to make the supplementary assumption that only non-metallic rings of a special type exhibit such tendency. It is suggested that the origin of complex compounds may be represented on an analogous principle, co-ordinative affinity arising as a result of the tendency towards saturation of non-dissociating, non-metallic atomic skeletons.
T. H. P.

**Quanta of the Ideal Monatomic Gas.** K. SCHAPOSCHNIKOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 105—124).—A mathematical paper, in which the quantum theory is applied to gases at high and at low temperatures. T. H. P.

**Chemical Constants of some Diatomic Gases.** J. R. PARTINGTON (*Phil. Mag.*, 1922, [vi], **44**, 988—993).—The investigations of Sackur (cf. A., 1913, ii, 128), and Tetrode (*Ann. Physik*, 1912, [iv], **38**, 434; **39**, 225) on the chemical constants of monatomic gases have been extended to the case of a hypothetical diatomic molecule. In the first case considered, the gas molecule is assumed to consist of two identical atoms rigidly attached to each other at a fixed distance apart. The method of calculation is based on generalised statistical mechanics, and it is shown that the following equation holds over a certain range of temperatures, $C=2\cdot5\log M+2\log K+12\cdot730$, where $K$=radius of gyration and $M$ the molecular weight. This gives values for the chemical constants $C_{O_2}=1\cdot001$, $C_{N_2}=0\cdot904$, and $C_{H_2}=-2\cdot255$. On account of the very small mass and diameter of the hydrogen molecule, hydrogen should behave in a manner intermediate between that of a monatomic and a diatomic gas. In the second case, that of two different atoms rigidly bound together, it is necessary to add log 2 to the above equation, and $C_{CO}=1\cdot205$, and $C_{NO}=1\cdot263$. These results are in all cases of the right order. W. E. G.

**A New Apparatus for Washing Gases.** A. ERNST (*Chem. Listy*, 1922, **16**, 274—276).—The tube leading the gas to be purified

into the washing bottle is surrounded by a long spiral, along which the gas has to make its way and is thus well washed. The tube leading in the gas and the spiral are easily removed from the vessel.

W. T.

**Protection of Brass Weights.** J. J. MANLEY (*Phil. Mag.*, 1922, [vi], **44**, 948—950).—The method introduced by Faraday for protecting iron from rust has been employed for protecting brass weights. A satisfactory method of procedure is to cover the weight with a thin film of linseed oil, and heat it, appropriately supported in a covered " vitreosil " crucible or closed muffle, until the weight assumes a golden tint. The protecting film which is formed is tough and may be polished. The weight of 1 sq. cm. of normal film is 0·00005 gram.

W. E. G.

**Lecture Experiments with Hydronitric [Hydrazoic] Acid and the Trinitrides [Azides].** A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2116—2119).—A series of lecture experiments with azoimide is described which includes the following. *Nitridation of hydriodic acid :* 5 c.c. of hydriodic acid (*d* 1·5) are placed in a 15 cm. test-tube and 1 c.c. of 1% hydrazoic acid is added when both iodine and nitrogen are liberated according to the equation $N_3H+2HI=NH_3+N_2+2I$. This experiment illustrates the similarity between hydrazoic acid and hydrogen peroxide. *Nitridation of hydrochloric acid :* 5 c.c. of hydrochloric acid are treated with 1 c.c. of 1% hydrazoic acid and raised to the boiling point for one minute; the contents of the tube are then poured into 2½ litres of water containing starch and potassium iodide, when the free chlorine liberates iodine. The reaction is represented by the equation $N_3H+2HCl=NH_3+Cl_2+N_2$. *Formation of potassium manganate by the action of potassium azide on manganese dioxide :* 0·5 gram of finely powdered potassium azide and 0·5 gram of manganese dioxide are mixed and gently heated in a 100 c.c. porcelain crucible covered by a 200 c.c. crucible. The reaction is violent and proceeds with a hissing noise and the emission of numerous sparks. When the reaction has moderated, the larger crucible is removed and the heating continued for a short time. After cooling the mass, it is thrown into 2½ litres of water, when the green solution produced speedily changes to that of a permanganate solution. In this experiment it is advisable that the operator should not come too close to the crucible at the commencement of the experiment. *Detonation of silver azide by means of a fuse consisting of paper impregnated with potassium azide:* Silver azide, prepared by adding a dilute solution of silver nitrate cautiously to 25 c.c. of a 1% solution of hydrazoic acid, filtering and washing with water, is made into a thin disk 18 mm. diameter and 1 mm. thick, while still moist. This is then stuck on a piece of filter-paper prepared as follows : a strip 0·5—1·0 cm. wide and 0·25—0·50 metre long is painted on a filter-paper by means of a small brush dipped in a 5% aqueous solution of potassium azide and dried. The disk of of ·er azide is attached to one end of the strip and the whole value ·ghly dried. The dried paper is then suspended and a glowing

splint brought in contact with the end of the strip removed from the silver azide; the combustion gradually progresses toward the silver azide, which finally detonates with a sharp report. J. F. S.

## Inorganic Chemistry.

**Diffusion of Hydrogen and Helium through Silica Glass and other Glasses.** G. A. Williams and J. B. Ferguson (*J. Amer. Chem. Soc.*, 1922, **44**, 2160—2167).—The rate at which hydrogen and helium, respectively, leak into evacuated tubes of silica glass, pyrex glass, and Jena glass has been determined at a series of temperatures and pressures. It is shown that silica glass is permeable to hydrogen at high temperatures. The permeability is proportional to the gas pressure and is an exponential function of the temperature. It becomes appreciable at 300°. Silica glass is similarly permeable to helium, and this is easily measurable at 182°. At 500°, the permeability for helium is about twenty-two times that for hydrogen. Neither pyrex glass nor Jena combustion glass was found to be permeable to hydrogen, but apparently hydrogen reacts with pyrex glass causing it to blacken. At 610°, pyrex glass is permeable to helium. The permeabilities of a number of samples of glass have been determined and the results compared with those of Wüstner (*Ann. Phys.*, 1915, [iv], **46**, 1095) and others. J. F. S.

**The Solubility of Oxygen in Various Organic Solvents.** Franz Fischer and Georg Pfleiderer (*Z. anorg. Chem.*, 1922, **124**, 61—69).—The solubility was determined by pumping the gas from the saturated solution by means of a mercury–air pump and measuring the amount obtained. The results embodying the solubility of oxygen in sixteen organic solvents are tabulated; the specific gravities and vapour pressures are also given. W. T.

**A New Form of Ozoniser.** H. Němeček (*Chem. Listy*, 1922, **16**, 276).—Two stout copper wires serve as electrodes in a horizontal glass cylinder, the arrangement being such that the distance between the electrodes can be varied. The energy can be obtained by means of a Rhumkorff's coil or an electric machine. W. T.

**Hydrophobic and Hydrophilic Sols of Sulphur.** H. Freundlich and P. Scholz (*Koll. Chem. Beihefte*, 1922, **16**, 234—266).—The behaviour of the hydrophobic and several hydrophilic sols of sulphur has been compared. As a markedly hydrophile sol, that investigated by Odén, and prepared by the interaction of hydrogen sulphide and sulphur dioxide, and by the decomposition of thionic acids, has been considered, and as a hydrophobe sol, that prepared by Weimarn by pouring an alcoholic

solution of sulphur into water, is considered. The Weimarn sulphu sol has been shown to be completely hydrophobic; it is negativel charged and is coagulated by electrolytes according to the genera laws concerning the coagulation of hydrophobic sols, namely, th strong influence of the absorbability and valency of the kations the strong effect of the hydrogen-ion, and the slight effect of th hydroxyl-ion. The sols may only be prepared in relatively smal concentrations, the coagulum is not peptised by washing wit water, and the sols may be preserved for a day or two only. I keeping with Odén's results, the coagulation of Odén's sol is markedl different from that of Weimarn's sol, as is demanded by its greate hydrophilic behaviour. The difference is mainly shown in th following points: (i) alkali salts have a ten to twenty times weake coagulating action than with Weimarn's sol; (ii) the lyotropi series of the kations is well defined; lithium-ions have a very weal coagulating action, whilst sodium-, potassium-, rubidium-, an cæsium-ions are markedly and increasingly stronger; (iii) acid have a still weaker coagulating action than the alkali salts; (iv) alkalis convert the Odén sol into one which has similar properties to the hydrophobic Weimarn sol. The assumption that the micellæ of Weimarn's sol consist of λ-sulphur and those of Odén's sol of μ-sulphur is insufficient to explain these differences; for neither the behaviour towards acids nor that towards bases is in the least explained by the above assumption, whilst a very possible explanation is that Odén's sol contains pentathionic acid, whereas Weimarn's sol does not. The presence of pentathionic acid in Odén's sol is proved by the following data: (i) the acid can be detected in the filtrate from coagulated sulphur by the fact that on the addition of alkali more sulphur is deposited; (ii) prolonged action of alkali on coagulated sulphur or sulphur micellæ brings about the formation of thiosulphate; this action is brought about by ammonia without the sulphur itself being markedly attacked. It is probable that the pentathionic acid is adsorbed in the sulphur particles, since this substance is very difficult to remove by washing. The quantity of pentathionic acid bound to the sulphur is found to be 0·1—0·7 millimol. per gram of sulphur. The influence of pentathionic acid on the stability of Odén's sol is explained as follows. This acid has a constitution which is closely related to that of water and sulphur and therefore it facilitates the formation of micellæ, which, in addition to sulphur and pentathionic acid, contain large quantities of water. The greater water content of Odén's sol is manifested by its greater transparency when compared with Weimarn's sol of equal sulphur content. The micellæ are to be represented in Odén's sol by the formula $\boxed{\begin{matrix} S\mu \\ S_5O_6H_2 \\ H_2O \end{matrix}} S_5O_6''$, and in Weimarn's sols by $\boxed{\begin{matrix} S\lambda \\ H_2O \end{matrix}}'$. The structure of the micellæ of Odén's sol explains the behaviour on coagulation as regards the following points: (i) alkalis decompose the pentathionic acid, whereby the loose combination

between the sulphur and water is also disturbed and converted into one which is similar to that of the Weimarn sol; (ii) acids have such a feeble coagulating power because they increase *the stability of the pentathionic acid and* produce more pentathionic acid from the pentathionates which may be present. The structure also is in keeping with the fact that hydrogen sulphide has an action on the sol similar to that of the alkalis; that is, it converts it into an hydrophobic sol which is much less stable because the pentathionic acid is decomposed by hydrogen sulphide with separation of sulphur. Further, sols of the same nature as Odén's sol are obtained by reactions which produce both sulphur and pentathionic acid; for example, the decomposition of sulphur monochloride by water: $5S_2Cl_2+6H_2O=5S+H_2S_5O_6+10HCl$. The stability of Odén's sol, which is due to pentathionic acid, does not depend on the charge of the micellæ. Whether or no Odén's sol contains S$\mu$ cannot be definitely answered, although the yellow colour of the sol makes it extremely likely that this variety of sulphur is present. J. F. S.

**The Existence of Sulphur Tetroxide.** FRIEDRICH MEYER, GUSTAV BAILLEUL, and GERHARD HENKEL (*Ber.*, 1922, **55**, [*B*], 2923—2929).—The experiments described owed their origin to a desire to examine Berthelot's sulphur heptoxide more fully, and as a considerable quantity of the product was desired, the original method was modified by submitting a current of sulphur dioxide and oxygen to the silent electric discharge instead of working with a fixed volume of the gases. Contrary to Berthelot's statements, the product which is formed does not appear to have an appreciable vapour tension even at 20°. The crystalline substance described by Berthelot is only formed when analysis shows that sulphur trioxide is present in excess. On the other hand, an amorphous product is obtained the analyses of which sometimes agree with the formula, $S_2O_7$, but sometimes show more oxygen than is required by this expression. The latter substance has been prepared in a specially designed discharge tube (which is figured in the original), which is so constructed that it is sufficiently small and light to be weighed on an analytical balance, that it can be evacuated and kept vacuous, and has little dead space. The material, thus prepared in the tube from sulphur dioxide and oxygen, is weighed and analysed in situ. For the latter purpose, it is treated with an aqueous solution of potassium iodide with which, at a sufficiently low temperature, it reacts with unexpected slowness and with the liberation of a very small proportion of oxygen. The latter is measured together with the liberated iodine and sulphuric acid. The highest stage of oxidation yet reached corresponds with the formula, $SO_3,2SO_4$. The authors, however, do not consider that this product represents the most highly oxidised form of sulphur which is possible, since in their work up to the present the imparted energy has not been sufficiently great in proportion to the volume of gas employed.

It appears possible that Berthelot's sulphur heptoxide is a

mixture of sulphur trioxide and sulphur tetroxide in equimolecular ratio. H. W.

**The Isotopes of Selenium and some other Elements.** F. W. Aston (*Nature*, 1922, **110**, 664).—Very satisfactory mass-spectra have been obtained in the case of selenium by vaporising the element in the discharge tubes. Selenium is shown to consist of six isotopes, giving lines at 80, 78, 76, 82, 77, and 74, respectively, in decreasing order of intensity. The results agree with the atomic weight as determined by chemical methods, and measurement of the lines shows no detectable deviation from the whole-number rule. The mass spectra of cadmium and tellurium could not be obtained by this method, but the experiments have incidentally shown that chlorine has no isotope of mass 39, and that aluminium is a simple element of mass 27. Two new isotopes of xenon, 124 and 126, making nine in all, are found to exist in minute amounts. The first of these is isobaric with tin, and the selenium lines 78, 80, and 82 are isobares of krypton; it is noted that all isobares so far discovered have even atomic weights. A. A. E.

**Action of Compounds of Nitric Oxide and Hydroxylamine on Trisodium Arsenite.** A. Gutmann (*Ber.*, 1922, **55**, [*B*], 3007—3012).—The oxidation of sodium arsenite to arsenate by sodium benzenediazoxide (which is not effected by the *iso*-diazoxide) has been attributed previously to the presence of a reactive, labile quadrivalent oxygen atom (A., 1912, i, 397; 1915, i, 127); an extension of the observations to a series of derivatives of nitric oxide and hydroxylamine indicates that sodium arsenite is a specific reagent for active oxygen.

Nitric oxide oxidises sodium arsenite in accordance with the equation: $2NO + Na_3AsO_3 = N_2O + Na_3AsO_4$; a similar change occurs when an excess of sodium arsenite is added to a solution of nitric oxide in freshly prepared, strongly alkaline potassium sulphite solution. Nitrosobenzene does not react with sodium arsenite at the atmospheric temperature but at the temperature of the boiling water-bath gives azoxybenzene and sodium arsenate. The constitutions $\begin{array}{c}N\cdot O\\ \mid\ \ \|\!|\\ N\cdot O\end{array}$ and $\begin{array}{c}Ph\cdot N\cdot O\\ \mid\ \ \|\!|\\ Ph\cdot N\cdot O\end{array}$, are suggested for nitric oxide and nitrosobenzene, respectively. Sodium nitroprusside does not appear to react with sodium arsenite. With hydroxylamine, the reactions $NH_2\cdot OH + Na_3AsO_3 = Na_3AsO_4 + NH_3$ and $3NH_2\cdot OH = NH_3 + N_2 + 3H_2O$ occur concurrently. β-Phenylhydroxylamine gives sodium arsenate, aniline, and azoxybenzene, $4NHPh\cdot OH + Na_3AsO_3 = Na_3AsO_4 + 2NH_2Ph + O{<}\begin{array}{l}NPh\\ \mid\\ NPh\end{array} + 2H_2O$, whereas the isomeric *p*-aminophenol is inactive. β-Ethylhydroxylamine, on the other hand, appears to give only arsenite and ethylamine. Dimethylaniline-*N*-oxide and sodium arsenite readily yield dimethylaniline and sodium arsenate. Quinine-*N*-oxide similarly gives quinine and sodium arsenate; the two oxides are therefore peroxidic. H. W.

**Properties and Structure of Pernitric Acid.** IV. TRIFONOV (*Z. anorg. Chem.*, 1922, **124**, 123—135).—Pernitric acid is formed by the action of hydrogen peroxide on an acidified nitrite solution; low temperature and low concentration are not essential for its formation. Above 70°, it decomposes rapidly. The per-acid can be estimated by the addition of potassium bromide in dilute solution, and the liberated bromine estimated by means of a potassium iodide solution. The author finds that the reaction of formation is represented by the equation $2HNO_2+3H_2O_2+(n-1)H_2O=N_2O_8,nH_2O+3H_2O$, and not as given by Raschig (*Ber.*, 1907, **40**, 4585) or Schmidlin and Massini (A., 1910, ii, 498). It thus receives the formula $NO_2{\cdot}O{\cdot}O{\cdot}NO_2,nH_2O$. The reactions of pernitric acid with some organic compounds are given. W. T.

**Phosphorus.** W. MARCKWALD and K. HELMHOLTZ (*Z. anorg. Chem.*, 1922, **124**, 81—104).—The authors find the melting point of scarlet phosphorus to be 592·5±0·5°, and the critical temperature of the yellow modification to be 720·6°. Rapid cooling of phosphorus vapour deposits a mixture of the yellow and scarlet forms; slow cooling deposits the pure yellow modification. To explain this the authors assume that phosphorus vapour at 900° and 120 mm. pressure consists of $P_4$ molecules and 10% $P_2$ molecules. On cooling, the $P_2$ and $P_4$ molecules combine to form the complex molecules of scarlet phospborus and this is to a certain extent deposited. Slow cooling, however, allows the scarlet phosphorus vapour to change into the vapour of the yellow form. The phenomenon observed on cooling liquid scarlet phosphorus is explained as follows. The liquid contains molecules of yellow ($P_4$) and scarlet ($P_x$) phosphorus in equilibrium: $nP_4 \rightleftharpoons mP_x$. Above 592·5°, most of the molecules are $P_4$ and on rapid cooling these solidify, giving the yellow variety. Slow cooling allows of a change of equilibrium to the right and therefore a deposit of the scarlet form on solidification. It is shown that the crystals isolated from a melt of the scarlet variety are identical with Hittorf's phosphorus. Black phosphorus changes into the scarlet form on being heated at 575°. W. T.

**The Toxic Properties of Commercial Ferrosilicon.** N. KURNAKOV and G. URASOV (*Z. anorg. Chem.*, 1922, **123**, 89—131).—Commercial ferrosilicon has been found to evolve poisonous and explosive gases. The alloys containing about 50% silicon, which is attacked by water, are very dangerous. The authors found that a solid phase of variable composition, *lebeauite,* makes its appearance in iron–silicon alloys with 33·4 to 100% by weight of silicon; lebeauite solidified at 1245°. Lebeauite can form ternary and quaternary solid solutions with phosphorus and aluminium. The ternary solid solutions (Fe,Si,P, and Fe,Si,Al) of lebeauite are stable towards water. The quaternary solution (Fe,Si,Al,P) is, however, attacked by water, phosphine being evolved. Ferrosilicon with less than 33·4% silicon in γ-iron can dissolve phosphorus and aluminium to the extent of 1·7% and 3%, respectively.

These ternary and quaternary solid solutions resist the action c water. Calcium phosphide will not dissolve in solid or liqui ferrosilicon. W. T.

**The Mechanism of the Formation of Silane from Magnesium Silicide. I.** ROBERT SCHWARZ and ERICH KONRA (*Ber.*, 1922, **55**, [*B*], 3242—3252).—The decomposition of magnesiu silicide by aqueous hydrochloric acid leads ultimately to the prc duction of a solid, white substance, $H_2Si_2O_3$, which shows all th properties of dioxodisiloxan. The substance, however, cannot b a primary product of the decomposition of the silicide, but is t be regarded as the final result of a series of intermediate reaction which cannot be followed in purely aqueous solution. Attempt are therefore made to arrest the reaction at intermediate stage by replacing the water to a greater or less extent by alcohol. Unde these conditions, monosilane is not evolved during the first perio of the action, and the solid product contains magnesium, whic cannot be removed by washing, but is free from chlorine. It is colourless substance (the usual brown tint is due to admixed ele mentary silicon) which explodes on contact with air, yieldin silicon and silicon dioxide, is decomposed by water, decolorise potassium permanganate and alcoholic bromine, and reduces silve nitrate. Analysis of it gives the ratio Si : Mg : H=1 : 2 : 2. Th primary hydrolysis of magnesium silicide may therefore be expresse by the equation: $Mg{:}Si{:}Mg+2H{\cdot}OH=H_2Si(Mg{\cdot}OH)_2$. In thes circumstances, not more than 15% of the silicon actually present i found in the solid product, whilst also none escapes as monosilane The remainder is found as a stable alcohol sol of silicic acid. A second reaction must therefore have occurred, possibly in accord ance with the scheme: $Mg_2Si+4HCl+2H_2O=4H_2+2MgCl_2+SiO_2$ whereby account is rendered of the evolution of hydrogen. Ap proximately 10% of the magnesium silicide is decomposed ir accordance with the first and about 90% in accordance with the second equation.

Many attempts have been made by varying the concentration of the alcohol and shortening the period of the action of the acid on the silicide to isolate other compounds intermediate between the primary product and the ultimate silicoformic anhydride. With increasing dilution of the alcohol, the production of silanes increases, but very little definite information is afforded by analysis of the solids. They can only be regarded as mixtures formed by further hydrolysis of the primary product, which they resemble in their ready inflammability on exposure to air. It appears probable that the initial product suffers further hydrolysis in two directions such as are suggested by the schemes: $SiH_2(Mg{\cdot}OH)_2+2H{\cdot}OH=2Mg(OH)_2+SiH_4$ and $SiH_2(Mg{\cdot}OH)_2+H_2O+4HCl=2MgCl_2+2H_2O+SiH_2O+2H_2$.

Magnesium silicide is prepared by igniting an intimate mixture of finely-divided, ignited quartz and magnesium powder in an atmosphere of hydrogen and mechanical separation of the crystals of the silicide from the mixture. The crude product is freed from

admixed magnesium by the action of ethyl bromide and anhydrous ether. The purified material is a uniform, steel-blue, crystalline powder which contains traces of amorphous silicon and iron silicide. The apparatus used in studying the decomposition of the silicide is fully figured and described in the original. H. W.

**Pressure of Saturated Carbonyl Chloride Vapour.** N. I. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 235—249).—The vapour pressure of carefully purified carbonyl chloride has been measured at a number of temperatures ranging from 12·6° to −99°. The pressure has the value 889·2 mm. at 12·6°, and diminishes rapidly with fall of temperature to 540·4 mm. at −0·41°, and then continually more slowly; at −19·43°, the value is 232·2 mm. and at −94·2° a few tenths of a millimetre. T. H. P.

**Interaction of Carbon Tetrachloride and Fuming Sulphuric Acid.** A. I. LEPIN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 1—17).—The author has investigated the mechanism of the formation of carbonyl chloride and chlorosulphonic acid from carbon tetrachloride and fuming sulphuric acid (cf. Schützenberger, *Annalen*, 1870, **154**, 375; Armstrong, *J. pr. Chem.*, 1870, [ii], **1**, 246; Erdmann, A., 1893, i, 681). If the fuming acid contains 45% of dissolved sulphur trioxide, corresponding with the formula $H_2S_2O_7$, the reaction is expressed by the equation, $CCl_4+H_2SO_4,SO_3=COCl_2+2SO_3HCl$. If less than 45% of dissolved trioxide is present, so that the acid may be regarded as a solution of fuming in monohydrated acid, the fuming acid acts as above, the excess of monohydrate remaining together with the secondary product, chlorosulphonic acid. Finally, if the dissolved sulphur trioxide exceeds 45%, the acid may be considered as a mixture of pyrosulphuric acid with sulphur trioxide. In this case, part of the carbon tetrachloride reacts according to the equation $CCl_4+H_2SO_4,SO_3=COCl_2+2SO_3HCl$, and part according to $CCl_4+2SO_3=COCl_2+S_2O_5Cl_2$; both these reactions proceed quantitatively. T. H. P.

**Reaction between Potassium Azide and Iodine in the Presence of Carbon Disulphide.** A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2106—2116).—Potassium azide reacts with iodine in the presence of carbon disulphide, with the formation of potassium iodide and the liberation of nitrogen. The first stage in this reaction consists in the formation of potassium azidodithiocarbonate, $KS{\cdot}CS{\cdot}N_3$, by interaction of potassium azide and carbon disulphide, as expressed by the equation $KN_3+CS_2=KS{\cdot}CS{\cdot}N_3$. This reaction is irreversible, consequently there is no regeneration of carbon disulphide after it has once reacted. The second stage consists in the reaction between potassium azidodithiocarbonate with iodine, which results in the precipitation of azidocarbon disulphide $S_2(CS{\cdot}N_3)_2$ according to the equation $2KS{\cdot}CS{\cdot}N_3+2I=S_2(CS{\cdot}N_3)_2+2KI$. The halogenoid substance azidocarbon disulphide liberates triatomic nitrogen from potassium azide, with resultant evolution of ordinary nitrogen, as shown by the equations $2KN_3+S_2(CS{\cdot}N_3)_2=2KS{\cdot}CS{\cdot}N_3+2N_3$; $2N_3=3N_2$.

Combination of these equations with the preceding one leads to the simple expression of the final result obtained when carbon disulphide, potassium azidodithiocarbonate, or azidocarbon disulphide, in relatively small amount, is brought into contact with a solution containing potassium azide and iodine. These results have been confirmed by iodometric and nitrometric determinations: $2KN_3+2I=2KI+3N_2$. J. F. S.

**Potassium Azidodithiocarbonate.** A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2315—2320; cf. preceding abstract; Sommer, A., 1916, ii, 29).—Potassium azidodithiocarbonate may be prepared by the action of carbon disulphide on an aqueous solution of potassium azide at 40°. It is obtained in colourless, deliquescent crystals, which decompose quantitatively when gently heated, yielding potassium thiocyanate, sulphur, and nitrogen. When rapidly heated, the substance explodes, with the formation of potassium sulphide, carbon dioxide, and sulphur dioxide and trioxide in addition to the above. Solutions of the salt when treated with various oxidising agents or when electrolysed yielded azidocarbon disulphide $(SCSN_3)_2$. The authors confirm the structure, K·S·CS·N⁚N⁚N, as assigned to it by Sommer (*loc. cit.*). W. G.

**Melting and Freezing Point of Sodium Chloride.** JOHN BRIGHT FERGUSON (*J. Physical Chem.*, 1922, **26**, 626—630).—The melting point and freezing point of sodium chloride have been determined by means of a platinum–platinum-rhodium thermo-element. As the mean of a number of experiments, the value 803·1° is found for the freezing point and 803·4° for the melting point. The author recommends the value 803°±1° as the best value for the freezing point. J. F. S.

**The Properties of Ammonium Nitrate. IV. The Reciprocal Salt-pair, Ammonium Nitrate and Sodium Chloride.** EDGAR PHILIP PERMAN (T., 1922, **121**, 2473—2483).

**Colloidal Calcium Hydroxide.** M. VON GLASENAPP (*Kolloid Z.*, 1922, **31**, 195—196).—Two varieties of colloidal calcium hydroxide have been obtained from a marly dolomite of the composition CaO 22·75%, MgO 15·50%, $Al_2O_3$ 7·68%, $Fe_2O_3$ 1·87%, $SiO_2$ 15·27%, $CO_2$ 34·83%, $H_2O$ 1·81%. The dolomite was burnt at 720—780° until the magnesium carbonate was entirely decomposed and the calcium carbonate half decomposed. After the burnt product had been kept for twelve hours in water, the two colloidal varieties of calcium hydroxide were microscopically visible. The primary product separates first from solution as small droplets which grow speedily, and pass into the secondary product which forms agglomerates of drops having the appearance of a cell network. Both colloids are optically isotropic but strongly refracting. In reflected light, the primary colloid is light blue and the secondary bright orange in colour. The secondary colloid does not maintain the colloidal state very long, but passes into crystalline calcium hydroxide. J. F. S.

**Valency. XVI. The Ammonia Compounds of Calcium Haloids.** GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1922, **123**, 31—42).—The methods of investigation were as previously communicated by the author (A., 1920, ii, 293 and 318). The following ammonia compounds were found to exist in the stable state :—$CaCl_2,8NH_3$; $CaCl_2,4NH_3$; $CaCl_2,2NH_3$; $CaCl_2,NH_3$; $CaBr_2,8NH_3$; $CaBr_2,6NH_3$; $CaBr_2,2NH_3$; $CaBr_2,NH_3$; $CaI_2,8NH_3$; $CaI_2,6NH_3$; $CaI_2,2NH_3$, and $CaI_2,NH_3$.

These determinations were carried out at various temperatures ranging from $-80°$ to 230°. The isothermal curves pressure–composition are given. W. T.

**The Solubilities of Calcite and Aragonite.** HANS L. J. BÄCKSTRÖM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 11, 1—11).—An account of work published more fully elsewhere (A., 1921, ii, 317). E. H. R.

**Setting and Velocity of Solution of Burnt Gypsum.** P. P. BUDNIKOV and JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 235—247).—The authors have investigated the velocities of dissolution of gypsum after the latter had been heated at various temperatures, the concentrations being determined at different stages of the dissolution by means of conductivity measurements. For the samples which have been heated at 115° and 125°, the conductivity and hence the solubility increases rapidly to a point corresponding with a solution considerably supersaturated with respect to $CaSO_4,H_2O$, and afterwards diminishes, at first rapidly and then slowly, but still indicates a certain degree of supersaturation after twenty-four hours. Supersaturated solutions are obtained also with gypsum heated at 400°, but not when a temperature of 500° is reached. In so far as the setting of gypsum is conditioned by crystallisation from supersaturated solutions, the temperature at which "dead-burnt" gypsum is formed may therefore be assumed to be about 450°.

Burnt gypsum may be regarded as consisting of two components, one soluble, which dissolves readily, and the other relatively insoluble. The solubility of samples which have been burnt at temperatures between 500° and 800° is rapid at first, this being explained by the presence of appreciable proportions of the soluble modification in dead-burnt gypsum.

The time occupied by dissolution does not furnish an exhaustive explanation of the disappearance of the ability of gypsum to set, and the authors suggest that the presence of the insoluble component in the interstices of the crystals prevents the latter from growing. T. H. P.

**The Silicates of Strontium and Barium.** PENTTI ESKOLA (*Amer. J. Sci.*, 1922, [v], **4**, 331—375).—The author has determined the equilibrium diagrams of the binary systems $SrO–SiO_2$ and $BaO–SiO_2$, respectively, and also certain characteristics (crystalline system and habit, refractive indices and dispersion, cleavage and density) of the compounds and eutectics formed in these

systems. The corresponding diagram and characteristics in the case of the system $CaO-SiO_2$ are given for purposes of comparison. In the system $SrO-SiO_2$, compounds $2SrO,SiO_2$ and $SrO,SiO_2$ were found, and these, together with SrO, occurred in one form only, although the temperature of formation of the silicates was varied from the melting point down to about 900°. $SrO,SiO_2$ was found to be closely isomorphous and optically very similar to $\alpha CaO,SiO_2$. Its crystals are apparently hemimorphic and belong either to the dihexagonal pyramidal or monoclinic domatic class, probably the latter. In the system $BaO-SiO_2$, compounds $2BaO,SiO_2$, $BaO,SiO_2$, $2BaO,3SiO_2$, and $BaO,2SiO_2$ were found. Of these, $2BaO,3SiO_2$ and $BaO,2SiO_2$ were found to be isomorphous, of orthorhombic symmetry, forming a complete series of solid solutions. The melting-point diagram of this series is of Roozeboom's type I, without maximum or minimum, and the index of refraction varies continuously, but not linearly with the composition. Barium metasilicate, $BaO,SiO_2$, is not isomorphous with the calcium and strontium meta-silicates. It is optically biaxial, probably of orthorhombic symmetry, and forms no solid solutions with $\alpha CaO,SiO_2$, but a double compound, $2CaO,BaO,3SiO_2$ is formed, which decomposes on heating into $\alpha CaO,SiO_2$ and liquid. Crystals of the double compound are uniaxial and negative, are probably hexagonal, and show good cleavages in their prismatic zone. Neither strontium nor barium metasilicate forms with magnesium metasilicate a double compound analogous to diopside. Felspars analogous to anorthite are formed by both strontium and barium. Strontium felspar and anorthite resemble one another very closely in optical properties, and the two appear to be completely miscible. Barium felspar is monoclinic and readily forms Carlsbad twins of the contact type. J. S. G. T.

**The System Ammonium Sulphate–Glucinum Sulphate–Water at 25°.** HUBERT THOMAS STANLEY BRITTON (T., 1922, **121**, 2612—2616).

**Preparation and Properties of Magnesium Perchlorate and its Use as a Drying Agent.** H. H. WILLARD and G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 2255—2259).—The hexahydrate of magnesium perchlorate may be prepared by dissolving magnesia in perchloric acid, evaporating the solution until fumes of perchloric acid are evolved and crystallisation commences at the surface. The mass is then cooled to the ordinary temperature with the addition of sufficient water to keep the mass semi-fluid. The crystals are separated by centrifuging, redissolved in water, and crystallised. The hexahydrate, m. p. 145—147°, $d_4^{25}$ 1·970, is now deliquescent. The trihydrate is prepared by keeping the hexahydrate over phosphoric oxide at 20—25° for a month. The product has m. p. 145—147°, $d_4^{25}$ 2·044. The anhydrous compound is obtained by heating either hydrate at 170° in a current of dry air for some time and then at 250° for a short time. Magnesium perchlorate decomposes at 400° without melting, forming a mixture of the oxide and chloride. When moist gas is

passed over anhydrous magnesium perchlorate at a rate not greater than 5 litres per hour, it is found to be as efficient a desiccating agent as phosphoric oxide. The trihydrate is as efficient as the anhydrous salt at 0°, but much less so at higher temperatures. J. F. S.

**Crystal Structure of Cadmium Iodide.** RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1922, **44**, 2232—2236).—The crystal structure of cadmium iodide has been investigated by means of *X*-ray spectra and Laue photographs. It is shown that cadmium iodide is not hexagonal, as has generally been supposed, but trigonal. The unit parallelepiped contains one molecule, and the shortest distance between the centres of the cadmium and iodine atoms is 3·00 Å.U., which is exactly the sum of the radii of these atoms as found by Bragg (A., 1920, ii, 537). Because of the nature of the structure, the iodine atoms are also "in contact" on the Bragg hypothesis. The shortest distance between their centres is 4·21 Å.U., whilst Bragg's value of the diameter of this atom is 2·80 Å.U. This separation indicates that the atoms which are presumably similarly charged may be expected to be farther apart than Bragg's hypothesis requires. The structure may be divided into electrically neutral layers by passing planes parallel to the base midway between the cadmium atoms, and this may well account for the excellent basal cleavage of the crystal. J. F. S.

**The Ammoniates of Lead Haloids. Mixed Compounds and the Parent Salts.** WILHELM BILTZ and WILHELM FISCHER (*Z. anorg. Chem.*, 1922, **124**, 230—247).—The following ammoniates of the haloids of lead are described in literature: $PbCl_2,1·5NH_3$; $PbCl_2,2NH_3$; $PbBr_2,2NH_3$; $PbI_2,NH_3$; $PbI_2,2NH_3$; and $PbI_2,4NH_3$. The authors were able to show also the existence of the following: $PbCl_2,NH_3$; $PbCl_2,3·25NH_3$; $PbBr_2,NH_3$; $PbBr_2,3NH_3$; $PbBr_2,5·5NH_3$; $PbI_2,0·5NH_3$; and $PbI_2,5NH_3$. The method of investigation was the same as that employed in previous work (cf. Hüttig, A., 1920, ii, 293, 318; this vol., ii, 849. The authors regard the compound $PbCl_2,3·25NH_3$ or $4PbCl_2,13NH_3$ as a mixed compound of the salts $PbCl_2,8NH_3$, $PbCl_2,2NH_3$, and $2PbCl_2,3NH_3$. Similarly, $2PbBr_2,11NH_3$ is a compound of $PbBr_2,8NH_3$ and $PbBr_2,3NH_3$, and $2PbI_2,10NH_3$ a compound of $PbI_2,8NH_3$ and $PbI_2,2NH_3$. These mixed compounds are not characterised by great stability or by instability; methods of detecting their formation are desirable. W. T.

**Action of Ammonium Nitrate and of Aqueous Ammonia on Copper. Properties of Cupric Tetrammine Nitrite and Nitrate.** HENRY BASSETT and REGINALD GRAHAM DURRANT (T., 1922, **121**, 2630—2640).

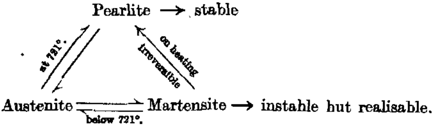
**The Solubility of Copper Hydroxide in Sodium Hydroxide Solutions.** G. SVENSEN MELBYE (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 8, 1—11).—The solubility of copper hydroxide in sodium hydroxide solutions between 2·65 and 6·6*N* increases at a linear rate with the concentration of sodium hydroxide according to the equation $[Cu(OH)_2]=0·045[NaOH]-0·095$.

The solutions were prepared by running a solution of copper sulphate very gently into the sodium hydroxide solution until turbidity appeared, they were then filtered and analysed. Assuming that a true solution of a cuprate is formed of the composition $Na_2Cu_2O_3$ and that its degree of dissociation is equal to that of sodium silicate, the ion product of the labile cupric acid, $H_2Cu_2O_3$, is found to be $K_1=0{\cdot}9\times10^{-17}$. For the hydrate $H_2CuO_2$ the ion product is $K_2=1{\cdot}3\times10^{-18}$. The solutions of sodium cuprate gradually deposit cupric oxide on keeping. E. H. R.

**The Composition of Scheele's Green.** G. BORNEMANN (*Z. anorg. Chem.*, 1922, **124**, 36—38).—The author finds that Scheele's green is not acid copper ortho-arsenite, $CuHAsO_3$, but a normal arsenite, $3CuO,As_2O_3,xH_2O$. The composition was found to vary with the method of preparation; the greater the excess of alkali employed the richer is the product in copper oxide. W. T.

**The Rate of Formation of some Nitrides.** G. TAMMANN (*Z. anorg. Chem.*, 1922, **124**, 25—35).—The rate of increase in thickness of the nitride was measured by the change in colour of the films. In the case of cerium, lanthanum, and a mixture of the two, the rate of increase of the film plotted against the logarithm of the time gave two straight lines cutting in each case at a definite temperature. The same applies to the metals in oxygen. The presence of moisture in the gases greatly accelerates their action. The film of nitride on iron protects the metal. Cobalt, nickel, molybdenum, tungsten, tantalum, and silicon do not change in an atmosphere of nitrogen at 700°; magnesium and calcium are converted into their grey nitrides. W. T.

**Honda's Conception of the A[1] Transformation and the Quenching of Steels.** MASUMI CHIKASHIGE (*Z. anorg. Chem.*, 1922, **124**, 59—60).—A theoretical paper, in which the author criticises the views of Honda (*Sci. Rep. Tohoku Imp. Univ.*, 1919, **8**, 181), and claims that a better interpretation is given by the following scheme :




W. T.

**The Ternary System Iron–Boron–Carbon.** R. VOGEL and G. TAMMANN (*Z. anorg. Chem.*, 1922, **123**, 225—275).—The authors discuss the results of Hannesen (A., 1915, ii, 464) and Tschischevsky and Herdt (A., 1917, ii, 372), who investigated the system iron–boron. The disagreement of their results is found to be due to differences in the rate of cooling. Rapid cooling (as carried out by the former) results in the separation of supersaturated mixed crystals. The

present authors carried out a systematic study of the ternary system iron–boron–carbon and their results are given in detail. Equilibrium sets in so slowly that the structure and properties of the iron–boron–carbon alloys depend to a large extent on the preliminary heating. The limit of the influence of boron on the structure was found to be 0·02%. W. T.

**The Constitution of Erdmann's Salt and its Derivatives.** E. H. Riesenfeld and R. Klement (*Z. anorg. Chem.*, 1922, **124**, 1—21).—The authors claim that Erdmann's salt, $[(NO_2)_4Co(NH_3)_2]R$, has the two ammonia molecules in the *cis*-position. They base their conclusions on the fact that (1) by the action of ethylenediamine the trinitro-ethylenediamine-monammine derivative is obtained, $[(NO_2)_3Co\,en\,NH_3]R$; (2) the dioxalato-diammine derivative, $[(C_2O_4)_2Co(NH_3)_2]R$, prepared from Erdmann's salt, could not be resolved into optical antipodes; (3) the non-resolvability again of the monoxalato-derivative, $[C_2O_4(NO_2)_2Co(NH_3)_2]$; (4) the ease with which the dichloro-derivative was prepared, $[(NO_2)_2Cl_2Co(NH_3)_2]$.

The oxalate group could not be replaced by the malonate radicle on account of the solubility and reducibility of the malonate. Methods of preparing the above derivatives are given. W. T.

**Preparation of Colloidal Solutions of Nickel and Cobalt Hydroxides and some other Compounds of these Metals.** O. F. Tower and Martha C. Cooke (*J. Physical Chem.*, 1922, **26**, 728—735).—Two methods are described for preparing colloidal suspensions of nickel hydroxide, one by dialysing a solution of nickel tartrate in the presence of an alkaline solution of potassium tartrate, and the other by treating a *N*/10-solution of nickel chloride with a little more than the equivalent quantity of a solution of potassium hydroxide, allowing the precipitated nickel hydroxide to settle, siphoning off the supernatant liquid, adding water, and repeating the process several times. Only very weak suspensions of cobaltous hydroxide could be obtained by these methods. Any solids obtained from the solutions referred to in a previous work on this subject (A., 1900, i, 587) are composed of nickel tartrate with potassium tartrate adsorbed in it. Glycerol does not prevent the precipitation of nickel hydroxide from aqueous solutions of nickel salts. In alcoholic solution, interesting transformations occur in the gel on keeping, and finally a solution is obtained from which nickel hydroxide cannot be precipitated by dilution with water. Colloidal solutions of nickel sulphide, which are readily formed in the presence of an alkaline solution of a tartrate, immediately decompose with precipitation of the sulphide on dialysing out the tartrate. J. S. G. T.

**Hydrated Oxides. IV.** Harry B. Weiser (*J. Physical Chem.*, 1922, **26**, 654—686; cf. this vol., ii, 575).—A continuation of previous work in connexion with the oxides of tin. It is shown that the so-called stannic and metastannic acids are not acids, but are hydrated stannic oxides the composition and properties of which are

determined by the conditions of formation. Stannic oxide, freshly prepared by precipitation from a solution of a stannic salt at the ordinary temperature, is a loose, highly hydrated mass which is readily peptised by dilute acids and alkalis, forming a colloidal solution, and is dissolved by concentrated acids and alkalis, forming salts. The oxide is more compact, less hydrated, less soluble, and less easily peptised the higher the temperature of formation. Freshly-prepared stannic oxide undergoes these changes on keeping at the ordinary temperature. Experiments on the peptisation by nitric acid of oxides prepared under different conditions show that the different products are not mixtures of varying amounts of a definite α-oxide peptisable by nitric acid with a definite β-isomeride which is not peptisable by nitric acid. Hydrated stannic oxides prepared at different temperatures or aged for varying lengths of time are chemical individuals which differ from each other in the size of the particles and the structure of the mass, and hence in their adsorbability and mordanting action, their ease of peptisation, and their solubility. There are no definite hydrates of stannic oxide. Salts of the general formulæ $SnR_4$ and $M_2SnO_3$ are formed by the action of concentrated acids and alkalis on newly-formed hydrated stannic oxide. Numerous oxy-salts and complex stannates and metastannates have been prepared by the action of acids and alkalis on different hydrated stannic oxides. These are not definite compounds, but are adsorption products, the composition of which is determined by the age of the hydrated oxide and the concentration of acid or base with which they were treated. Colloidal solutions of hydrated stannic oxide can be prepared by peptisation of the freshly-formed oxide with dilute acids or alkalis. The colloid ages slowly on keeping and rapidly on heating. Any number of colloidal solutions are possible, each differing from the others in the size of the hydrated particles and hence in their reactivity, adsorbability, and stability under given conditions. Hydrated stannic oxide adsorbs colloidal gold, silver, and platinum, forming purple masses, the most common of which is the gold compound, purple of Cassius. All these purple substances are colloidal in character, the composition varying with the conditions of formation. When freshly prepared, they are readily peptised by dilute acids and alkalis, but when aged by drying they are peptised but slightly even by concentrated reagents. A mixture of the hydrated oxides of iron and tin in certain proportions is soluble in dilute ammonia. The reason for this is that hydrated stannic oxide is peptised by the hydroxyl-ion, whilst ferric oxide is not, but colloidal stannic oxide adsorbs ferric oxide and carries it into colloidal solution as long as tin is present in excess. At the same time, hydrated ferric oxide adsorbs stannic oxide and tends to take it out of colloidal solution, so that when the former is present in large excess none of the latter remains peptised. Stannic oxide does not precipitate in the usual way from a solution of tin in nitric acid containing a suitable amount of iron. The reason for this is that hydrated stannic oxide peptised by nitric acid coagulates spontaneously, since the aged oxide is neither peptised nor dis-

solved by this acid. Ferric nitrate peptises the oxide both when newly formed and when aged. Hence if freshly-prepared stannic oxide is peptised either by ferric nitrate or by a suitable mixture of ferric nitrate and nitric acid, coagulation does not take place on keeping or boiling on account of the stabilising action of the strongly adsorbed ferric ion; but if the concentration of ferric ion in the nitric acid solution is too low, complete or partial coagulation takes place on keeping or boiling. Stannic oxide jellies are prepared by coagulation of colloidal solutions of the oxide with suitable concentrations of electrolytes. The results of the present investigation support the author's general hypothesis of the formation of jellies.

J. F. S.

**The Occurrence of Germanium in Cassiterite.** Assar Hadding (*Z. anorg. Chem.*, 1922 **123**, 171—172).—The author examined cassiterite from Finbo by means of the *X*-ray spectrograph and found it to contain the following elements: tin, tantalum, iron, manganese, germanium, and zinc. The intensity of the lines shows that the amount of germanium was less than that of manganese and more than that of zinc. A similar analysis of cassiterite from Mamacka gave like results. No germanium was indicated in cassiterite from Finland and Bohemia. W. T.

**Germanium Hydride.** Rudolf Schenck [with Albert Imker] (*Rec. trav. chim.*, 1922, **41**, 569—575).—The preparation of an alloy of germanium and magnesium could not be effected by the action of magnesium on germanium oxide, as the reaction is too violent. The germanium was obtained as oxide from argyrodite; this was purified by conversion into germanium silicofluoride, thence into sulphide, and finally into oxide. Reduction to the metal was then effected by heating in a stream of hydrogen, and an alloy was prepared by heating one part of the powdered germanium so obtained with two parts of magnesium powder in an atmosphere of hydrogen. The hydride, prepared by the action of hydrochloric acid on the alloy in a stream of hydrogen, was obtained pure by cooling to the temperature of liquid air. Small quantities of germanium chloroform were produced simultaneously with the hydride and condensed in a freezing mixture in the preliminary stages of cooling. The uncondensed gases were passed through silver nitrate solution and again through a tube cooled in liquid air, but were not completely freed from the hydride, which could still be detected by its nauseating odour and by the deposition of metallic germanium on porcelain when the gas was burnt. The hydride condensed to a white solid which was purified by sublimation, m. p. —165°, b. p. —126°/757 mm. Values for the vapour pressure from —164° to —125° are given. Three determinations of molecular weight by Regnault's method gave a mean value of 76·93, the theoretical value being 76·50. The gas readily decomposes into its elements on heating (cf. Paneth and Schmidt-Hebbel, this vol., ii, 776), and an analysis was carried out by passing it through a heated tube, the hydrogen formed being estimated in a eudiometer and the germanium weighed

as such. Three determinations gave 94·70% Ge and 5·29% H as mean values, the calculated percentages for $GeH_4$ being 94·73 and 5·27. The volume ratio of germanium hydride to the hydrogen obtained by its decomposition was found to be 1 : 2·05. The general reactions of the gas show that it is endothermic and analogous in properties to the hydrides of arsenic, antimony, tin, and bismuth (cf. Voegelen, A., 1902, ii, 401). H. J. E.

**Sulphide Sols. III. Sol Preparation by Hydrolysis.** F. V. VON HAHN (*Kolloid Z.*, 1922, **31**, 200—203; cf. A., 1921, ii, 577).—Fairly stable antimony pentasulphide sols may be prepared by the hydrolysis of the alkali salts of stibiothiosulphuric acid. The hydrolysis takes place extremely readily according to the equation $2Na_3Sb(S_2O_3)_3=Sb_2S_5+3Na_2SO_4+3SO_2+S$ (Szilágyi, A., 1920, ii, 207). The preparation is carried out as follows: a 0·5% solution of sodium antimony thiosulphate is kept until it commences to turn yellow and to show a definite Tyndall cone; it is then placed in a dialyser and washed with warm distilled water. After several hours' dialysis, the solution has taken on a deep red colour. The main point to be observed in the preparation is the rapid removal of the alkali sulphate. In the presence of sodium chloride the sol cannot be prepared, nor can a sol having a greater molecular concentration than 0·4 be obtained. Sols of one-tenth this concentration are stable for a few hours only. The sols prepared from the sodium salt are more stable than those prepared from either lithium or potassium antimony thiosulphate. Attempts to prepare arsenic pentasulphide sols by the hydrolysis of alkali arsenic thiosulphates failed entirely owing to the greater instability of these compounds. J. F. S.

**Complex Platinum Compounds. III. Molecular Rearrangements observed with Complex Platinum Compounds.** L. A. TSCHUGAEV and N. K. PSCHENICYN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 47—62).—The depolymerisation of bicomplex salts of the type $[Pt4A]PtX_4$ (where $A$=a molecule of ammonia, amine, organic sulphide, etc.), resulting in the formation of the monomeric type $[Pt2A,X_2]$ and in the accompanying transference of one-half of the total $A$ molecules from one platinum atom to another is frequently encountered among complex platinum compounds, but has not previously been observed with the simplest purely inorganic, in particular with the ammino-, complexes of platinum. This gap has now been filled by the authors, who show that tetra-amminoplatinous platinochloride (Magnus's green salt) is capable of undergoing depolymerisation in accordance with the scheme $[Pt4NH_3]PtCl_4=[Pt2NH_3,Cl_2]$, the chloride of Reiset's Base II being thus formed. The reaction is effected by cautious heating over a naked flame to 270°, and never proceeds to completion, part of the green salt decomposing with separation of metallic platinum.

Experiments have been made also with certain heterometallic bicomplex compounds, in which the platinum occurs only in the anion, $[PtX]_4$, whilst the kation is formed of another metal in com-

bination with a known number of *A* molecules giving the so-called neutral part of the complex: for example, $[M,nA]PtX_4$. If as the component *M* is taken an element such as silver, zinc, copper, mercury, etc., which, according to all the available data, holds molecules of ammonia, etc., less stably than does platinum, the transference of these molecules from the metal *M* to the platinum should take place with great readiness. With the amminosilver platinichlorides, the transference of ammonia from the silver to the platinum atom occurs at comparatively low temperatures: At 60—70°, monoamminosilver platinichloride yields, together with silver chloride, also (*a*) tetra-amminoplatinous platinichloride (Magnus's green salt), (*b*) chlorotriamminoplatinous platinichloride (Cleve's salt), and (*c*) *cis*dichlorodiamminoplatinum (Peyrone's chloride)

$$(a)\ [Pt4NH_3]PtCl_4 \longleftarrow [AgNH_3]_2PtCl_4 \longrightarrow {}^{NH_3}_{NH_3}\!\!>Pt<\!{}^{Cl}_{Cl}\ (c)$$

$$\downarrow$$

$$(b)\ [Pt3NH_3Cl]_2PtCl_4,AgCl$$

whilst at a higher temperature (100°) the last two compounds disappear and are replaced by *trans*-dichlorodiamminoplatinum (chloride of Reiset's Base *II*); in either case, the loss of ammonia is negligible. At all temperatures between 100° and 200°, diamminosilver platinichloride yields a new product, namely, tetra-amminoplatinous chloride (chloride of Reiset's Base I), the loss of free ammonia being considerable. At 100°, the only compound, besides silver chloride, accompanying the chloride of Reiset's Base I is Magnus's salt; at 150°, the chloride of Reiset's Base II also appears, whilst at 200° Magnus's salt disappears and the chlorides of Reiset's Bases I and II form the sole products. The Base II chloride, which appears in all cases at the highest temperatures, is evidently a secondary product formed from Magnus's salt.

When heated at 50—60°, diethylamminosilver platinichloride readily undergoes transformation into the analogues of the chloride of Reiset's Base I and Magnus's green salt, part of the ethylamine being liberated: $[Ag2NH_2Et]_2PtCl_4=2AgCl+[Pt4NH_2Et]Cl_2$ and $2[Ag2NH_2Et]_2PtCl_4=4AgCl+[Pt4NH_2Et]PtCl_4+4NH_2Et$. Under the same conditions, monoethylamminosilver platinichloride gives the analogues of Magnus's green salt and Peyrone's chloride, part of the original compound also decomposing with complete loss of the amine and formation of silver platinichloride.

Tetramminozinc platinichloride, $[Zn4NH_3]PtCl_4$, gives, at 111°, Peyrone's chloride, Magnus's green salt, and the chloride of Reiset's Base I. T. H. P.

**The Alkali-Ruthenium Double Sulphites.** HEINRICH REMY (*Z. anorg. Chem.*, 1922, **124**, 248—274).—The following definite double sulphites of ruthenium and the alkali metals were prepared, $K_2SO_3,Ru(OH)SO_3,3H_2O$; $K_2SO_3,3RuSO_3,6H_2O$(?); $7Na_2SO_3,2RuSO_3,7H_2O$; $7Na_2SO_3,2RuSO_3,9H_2O$; $3K_2SO_3,4RuSO_3,6H_2O$.

There were also obtained substances which on analysis did nc correspond with any simple formula, probably being mixtures of th above. The properties of the above double sulphites are give The author discusses the difficulties of analysis. W. T.

## Mineralogical Chemistry.

**The Examination of Naturally Occurring Gases. II.** I HENRICH [with G. PRELL] (*Ber.*, 1922, **55**, [*B*], 3021—3025).—Th method for the collection and examination of naturally occurrin gases has been simplified and extended (cf. A., 1920, ii, 767). Th gases from a number of springs have been analysed, since suc data appear to the author to form the most trustworthy basis fo a judgment as to the atmospheric or terrestrial origin of the wate Re-examination of the gas from a cold spring near Leupoldsdorf Bavaria, confirms the previous analysis (Henrich, *loc. cit.*), showin it to contain oxygen 13%; nitrogen and the rare gases being th only other constituents. The gas from a second spring situate about a hundred metres above the foregoing was also compose of the constituents of air, but with only 18·8% of oxygen. Th gas from a third spring was found to contain oxygen (18·2%) nitrogen (81·8%), argon, and neon (1·1%). Since the ratio o nitrogen to rare gas in these gases is approximately the same as i air, it appears that the latter in some unexplained manner has go below the water in the spring. The low oxygen content of th gases in comparison with that of air is explained by the greate solubility of oxygen than of nitrogen in water, so that a gas riche in nitrogen is evolved. The extent to which the air is depleted o its oxygen appears to depend on the pressure of the water in th spring. H. W.

**The Examination of Naturally Occurring Gases. III** F. HENRICH [with G. PRELL] (*Ber.*, 1922, **55**, [*B*], 3026—3030).— Analyses are given of the gases from a number of pools on th Luisenburg near Wunsiedel and Alexandersbad (Fichtelgebirge) o which one may be quoted

$H_2S$ (traces), $CO_2$ 3·1%, $O_2$ 1·7%, $CH_4$, 53·9%, $N_2$+rare gases 41·3%

Methane, carbon dioxide, and the small amounts of hydroge sulphide appear to owe their origin to a bacterium which is no completely identical with *Bacillus methanigenes*. Nitrogen and th rare gases must be derived originally from the air. H. W.

**Dopplerite. Studies in the Composition of Coal.** FRED ERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T. 1922, **121**, 2345—2362).

**Massive Troilite from Del Norte Co., California.** ARTHUR ...KLE (*Amer. Min.*, 1922, **7**, 77—80).—The bronze-tarnished

mineral (light greyish-brown when untarnished) resembles pyrrhotite, but differs from this in being non-magnetic and in being readily soluble in dilute sulphuric acid. Analysis of the soluble portion gave Fe 62·70, S 35·40% agreeing with the formula FeS; *d* 4·67. The mineral is thus identical with the meteoric troilite. It occurs with chalcopyrite and magnetite in serpentine, and has probably resulted by the action of hydrogen sulphide solutions on the magnetite. Troilite and pyrrhotite are regarded as distinct species, and the suggestion that pyrrhotite is FeS+S in solid solution (*A.*, *1912*, *ii*, *354*) is not accepted. The magnetic character of pyrrhotite suggests the formula $Fe_3S_4$ for the end-member of the series $Fe_nS_{n+1}$. L. J. S.

**Keeleyite, a new Lead Sulphantimonite from Bolivia.** SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1922, **74**, 101—103).—This occurs as radiating aggregates of acicular (perhaps orthorhombic) crystals with pyrites and quartz in the San José mine at Oruro. It is dark grey with bright metallic lustre and gives a greyish-black streak; *d* 5·21, *H* 2. Analysis by J. E. WHITFIELD gave:

| Pb. | Sb. | Cu. | Fe. | S. | Quartz. | Total. |
|---|---|---|---|---|---|---|
| 25·80 | 43·46 | 2·25 | 2·77 | 24·54 | (1·18) | 100·00 |

Deducting 8·15% of admixed sulphides, this gives the formula $2PbS,3Sb_2S_3$, corresponding with rezbanyite ($2PbS,3Bi_2S_3$). The compositions of the known lead sulphantimonites are represented on a triangular diagram. L. J. S.

**An Andorite-bearing Silver Ore from Nevada.** EARL V. SHANNON (*Proc. U.S. Nat. Museum*, 1922, **60**, art. 16, 1—5).—An ore specimen from Keyser mine, Nye Co., Nevada, shows rough prisms of andorite with pyrite and sphalerite in a gangue of rhodochrosite and quartz. Analysis I of the andorite gives, after deducting zinc and iron as sphalerite, the formula $PbAgSb_3S_6$. The crystals are usually altered and filled in a central cavity with a matted mass of fine fibres. Analysis II of this alteration product suggests the formula $Pb_2AgSb_3S_8$, and shows that there has been a removal of silver and antimony sulphides.

| | Pb. | Ag. | Fe. | Zn. | Sb. | S. | Total. |
|---|---|---|---|---|---|---|---|
| I ...... | 23·35 | 12·09 | 1·55 | 3·56 | 37·64 | 22·63 | 100·82 |
| II ...... | 45·14 | 7·78 | 2·72 | 1·56 | 23·22 | [19·58] | 100·00 |

The pale pinkish-buff rhodochrosite gave:

| MnO. | FeO. | CaO. | MgO. | $CO_2$. | Total. | $MnCO_3$. |
|---|---|---|---|---|---|---|
| 49·49 | 7·68 | 3·13 | 0·93 | [38·87] | 100·10 | 80·15 |

L. J. S.

**Sodium Carbonate Minerals from Lake Magadi, Kenya Colony.** P. WALTHER (*Amer. Min.*, 1922, **7**, 86—88).—The extensive trona deposit of Lake Magadi consists of an aggregate

of pale-yellow, bladed crystals up to 9 cm. in length. Analysis of an average sample with *d* 2·14 gave :

| $Na_2CO_3$. | $NaHCO_3$. | $H_2O$. | NaCl. | $Fe_2O_3$, $Al_2O_3$. | $SiO_2$. | CaO,MgO,$SO_3$. | Total. |
|---|---|---|---|---|---|---|---|
| 43·55 | 40·41 | 15·55 | 0·36 | 0·04 | 0·07 | traces | 99·98 |

agreeing with the formula $Na_2CO_3,NaHCO_3,2H_2O$. The mineral has evidently been formed by the action of carbon dioxide and water on sodium silicates, since the rocks in the neighbourhood show extensive bands of flinty silica and carbon dioxide issues from numerous cracks at the surface. The salt crusts of Little Magadi, a dry salt pan 25 miles to the south, consist of harder, bladed (monoclinic ?) crystals which on analysis proved to be pure sodium hydrogen carbonate. This, owing to ready loss of carbon dioxide and conversion into trona, has not hitherto been recognised as a mineral. It here owes its existence to the presence of a large excess of carbon dioxide, which issues from cracks in the soil and rocks with a hissing sound. Optical examination by E. T. Wherry detected only trona, but the material had evidently been altered in the meantime. A new mineral name for sodium hydrogen carbonate is therefore avoided for the present. L. J. S.

**Constitution of Thaumasite.** Edw. F. Holden (*Amer. Min.*, 1922, **7**, 12—14).—Calculations by the Lorentz-Lorenz formula of the molecular refractivity of thaumasite, directly and from its components, point to the presence of 2OH (rather than 4OH) in the formula $CaCO_3,CaSO_4,CaSiO_3,15H_2O$. L. J. S.

**Minerals from Ljubija, Bosnia.** Rudolf Koechlin (*Tsch. Min. Mitt.*, 1921, **35**, 1—12).—The iron-ore at Ljubija, near Prijedor, consists of crystalline-granular chalybite with impregnations of galena, pyrites, and chalcopyrite. Near the surface, the chalybite is altered to limonite, with which are various other secondary minerals. These, including the rarer species leadhillite, pyrochroite, and beudantite, are described. L. J. S.

**A New Mineral which Contains the Rare Earths as its Main Component.** F. Henrich [with G. Hiller] (*Ber.*, 1922, **55**, [*B*], 3013—3021).—*Weinschenkite* occurs in very small quantity in the Bavarian Oberpfalz in white, matted, globular deposits and in radiating needles on brown hæmatite from which it is readily detached. It appears to be mainly a hydrated phosphate of yttrium and erbium, $PO_4(Er,Y),2H_2O$; but indications of the presence of other rare earths have been obtained. The small amount available was insufficient for a complete analysis.

*Pseudowavellite*, also occurring in minute amount in the same locality, resembles wavellite in that it contains aluminium as its main component, with calcium oxide (13%), barium oxide, and strontium oxide (about 1%) and rare earths (2—3%). Erbium and yttrium appear to be present in addition, possibly, to the cerium earths. H. W.

**Supplementary Note on Ishikawaite, a New Mineral from Ishikawa, Iwaki Province.** YÛJI SHIBATA and KENJIRO KIMURA (*J. Chem. Soc. Japan*, 1922, **43**, 648—649).—The unnamed mineral from Ishikawa, of which an analysis was given (this vol., ii, 517), is now termed *ishikawaite;* the crystals are rhombic [$a:b:c=0{\cdot}9451:1:1{\cdot}147$]. K. K.

**Glauconite from Lewes, Sussex: Constitution of Glauconite.** A. F. HALLIMOND [with analysis by E. G. RADLEY] (*Min. Mag.*, 1922, **19**, 330—333).—A boring through the Gault at Iford Manor, near Lewes, struck the Greensand at a depth of 325 feet. The upper bed of this consists almost entirely of small grains of dark-green glauconite. The grains consist of a felted mass of minute, birefringent flakes with mean $n$ 1·62; $d$ 2·70. Analysis gave:

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. |
|---|---|---|---|---|---|
| 48·12 | 9·16 | 19·10 | 3·47 | 0·76 | 2·36 |

| $K_2O$. | $Na_2O$. | $H_2O$ at 105°. | $H_2O$ >105°. | Total. |
|---|---|---|---|---|
| 7·08 | 0·22 | 4·78 | 5·28 | 100·33 |

From this and a selection of earlier analyses, the formula is deduced as $R_2O,4(R_2O_3,RO),10SiO_2,nH_2O$, in which $Al_2O_3+Fe_2O_3$ and $FeO+MgO$ are regarded as mutually replaceable. In some cases, there is a considerable replacement of potassium by sodium, and the variety soda-glauconite is suggested. L. J. S.

**Structure and Composition of the Strathmore (Perthshire) Meteorite.** W. F. P. MCLINTOCK and F. R. ENNOS (*Min. Mag.*, 1922, **19**, 323—329).—Four stones were observed to fall along a track six miles in length on December 3, 1917; the largest weighed 9932 grams and the total weight was 13,255 grams. The structure is that of the intermediate chondrite group; $d$ 3·53. The bulk-analysis, deduced from analyses of the attracted and unattracted portions, is:

| Fe. | Ni. | Co. | Fe. | S. | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Cr_2O_3$. | $Fe_2O_3$. |
|---|---|---|---|---|---|---|---|---|---|
| 7·31 | 1·26 | 0·05 | 4·00 | 2·29 | 40·32 | 0·14 | 2·57 | 0·44 | 0·35 |
| FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | $P_2O_5$. | Cl. | Total |
| 12·99 | 0·29 | 1·84 | 24·96 | 0·11 | 0·90 | 0·17 | 0·23 | 0·03 | 100·25 |

From this is calculated the following mineral composition: felspar 10·93, ilmenite 0·27, chromite 0·65, magnetite 0·51, chlorapatite 0·56, olivine 41·13, bronzite 30·91, troilite 6·29, nickel-iron 8·62, water 0·17%. L. J. S.

# Analytical Chemistry.

**A Microcolorimeter and Nephelometer.** A. BAUDOUIN and H. BÉNARD (*Compt. rend. Soc. biol.*, 1920, **83**, 602—603).—A description of a miniature Duboscq colorimeter, of which the cups have a capacity of 2 c.c., and the tube an adjustment of 20 mm. The apparatus can also be used as a nephelometer or ultraphotometer, and, by replacing the ocular with a small, direct-vision spectroscope, can be converted into a spectroscope comparator.

CHEMICAL ABSTRACTS.

**Colorimeter.** ED. MOREAU and A. BONIS (*Ann. Falsif.*, 1922, **15**, 357—360).—The apparatus consists essentially of two graduated cylinders placed side by side in a suitable frame; one of these contains the test solution and the other the standard or comparison solution. The latter is admitted through a side tube at the bottom of the cylinder, this tube being connected with a tapped funnel or reservoir containing the solution. W. P. S.

**The Application of Coloured Glasses instead of Liquids in Colorimetric Researches.** KLAS SONDÉN (*Arkiv Kem. Min. Geol.*, 1922, **8** No. 7, 1—10).—Combinations of coloured glasses are used as standards in colorimetry. Coloured glasses suitable for this purpose may be prepared by dyeing the gelatin films on photographic plates from which the silver has been removed by treatment with thiosulphate. W. O. K.

**A New Apparatus for Exact Gas Analysis.** K. A. SCHALLER and W. BERNDT (*Chem. Ztg.*, 1922, **46**, 972—973).—The apparatus consists of a manometer, a measuring tube immersed in a water-jacket with air agitation, and a detachable absorption vessel with an adjustable mercury reservoir. The passage of the mercury from the manometer into the measuring tube is prevented by placing between them a U-tube containing at its lowest point either a constriction or a throttle cock. All the operations of gas analysis can be carried out in this apparatus except explosions, for which the absorption vessel is replaced by a eudiometer. The procedure for estimating carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, and the combustion of hydrogen, methane, and ethane is described. H. C. R.

**A Modified Methyl-orange Indicator.** KENNETH CLAUDE DEVEREUX HICKMAN and REGINALD PATRICK LINSTEAD (T., 1922, **121**, 2502—2506).

**Apparatus for Electrometric Titration.** W. E. GARNER and C. A. WATERS (*J. Soc. Chem. Ind.*, 1922, **41**, 337—338T).—The electrode vessel, which carries a small bulb, is attached to a rotating stirrer; two side tubes on the vessel are turned downwards and constricted at the ends. The bulb is convenient in the preparation of a calomel electrode. The side tubes are packed with asbestos, the

vessel is filled completely with electrolyte, and it is supported from the glass tube of the stirrer by means of a waxed cork. The metal used as an electrode is fused or waxed into a thin glass tube and attached by means of a small binding screw to the rotating spindle, electrical connexion being made through a small steel mercury cup to another binding screw. The outer electrode is of any convenient form; the turned-down side tubes on the electrode vessel make it possible to commence a titration with 5 c.c. of solution in the beaker.

W. P. S.

**Quantitative Analysis by Measurement of the Degree of Supersaturation.** ERNST FRITZ HÖPPLER (*Chem. Ztg.*, 1922, **46**, 957—958).—The time elapsing between the addition of a reagent and the formation of a precipitate or coloration can be utilised as an approximate quantitative measure of traces of substances in solution. The method is particularly applicable to water analysis. Sulphuric acid and calcium can be estimated in this way between the dilutions of 2·3 and 100 mg. per litre. Nitrous acid can also be estimated by this means when not in greater concentration than 0·5 mg. per litre.

H. C. R.

**The Rapid Estimation of Chlorine in Organic Compounds.** E. VOTOČEK (*Chem. Listy*, 1922, **16**, 248—249).—The author combines the method of Marcusson and Döscher (A., 1910, ii, 543) with his titration of chlorides against a mercuric salt in the presence of sodium nitroprusside as an indicator. The present author carries out the combustion in a funnel-shaped vessel of several litres capacity fitted with a stopcock. Since sufficient hydrogen is present in the molecule to convert all the chlorine into hydrogen chloride, the products of combustion are absorbed by water and titrated directly against mercuric nitrate. The estimation takes about an hour and a half.

W. T.

**Potassium Dichromate as a Standard in Iodimetry and the Estimation of Chromates by the Iodide Method.** WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1922, **44**, 2120—2130).—It is shown that titration of iodine with thiosulphate in dilute acid solutions gives results which are 0·1—0·3% higher, and more concordant than the results of titration in a neutral solution. The presence of air affects the titration of iodine with thiosulphate when the acidity of the solution is equivalent to 0·3*N*-hydrochloric acid or greater, causing too much thiosulphate to be required. An apparent excess of oxidising action of dichromate is caused by the titration of the iodine in a solution of too high an acid concentration. This can be corrected by the exclusion of air, but more easily by dilution to such an hydrogen-ion concentration that the presence of air will not interfere. Chromates may be estimated to within 0·1% by the iodide method under the proper conditions. Potassium dichromate as a standard for thiosulphate solutions agrees with pure iodine to within 0·1%, but gives a slightly lower value. Errors in the iodine standardisation leading to such a difference appear to be about as probable as errors in the dichromate standardisation.

A standard solution of potassium permanganate is not trustworthy as a standard for thiosulphate solutions. J. F. S.

**The Estimation of Sulphuric Acid as Barium Sulphate. Evidence of the Existence of a Complex Barium Sulphuric Acid.** D. BALAREFF (*Z. anorg. Chem.*, 1922, **123**, 69—82).—The sources of error in the estimation of sulphuric acid as barium sulphate are: (1) occlusion of salts by the precipitate, for example, barium chloride; (2) occlusion of the mother-liquor; (3) the formation of the complex ion $[Ba_5(SO_4)_6]$, and this leads to the chief error. The author isolated the potassium salt of this complex ion $[Ba_5(SO_4)_6]K_2$. The most accurate results are obtained when barium sulphate is precipitated slowly from a dilute, boiling solution acidified with hydrochloric acid. Crystals in the precipitate have various forms; the prismatic form corresponds with the simple salt $BaSO_4$. The chlorine content of barium sulphate is not caused by the salt $SO_4(BaCl)_2$. W. T.

**Application of Conductometric Titrations to Precipitation Analysis. V. Conductometric Titrations with Barium Salts.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 433—448).—Sulphates may be accurately titrated conductometrically by means of barium chloride in solutions as dilute as $0.001N$. The titration may be carried out more rapidly and exactly if alcohol is added to the solution than if an excess of barium sulphate is stirred in. The presence of mineral acids, aluminium, and calcium leads to low results, whereas the presence of iron salts generally causes the results to be too high. Nitrates in moderate amount do not interfere. The method is not applicable to the determination of sulphates in water owing to the presence of calcium.

Carbonates and chromates, as well as oxalates, tartrates, citrates, and malates in the presence of sufficient alcohol may all be titrated with barium chloride in a similar manner to sulphates, but phosphates, pyrophosphates, succinates, benzoates, and salicylates cannot be titrated by conductometric methods with barium chloride. A. R. P.

**Some new Volumetric Methods. (Estimation of Sulphate, Lead, Acids, and Ammonia.)** KARL JELLINEK and H. ENS (*Z. anorg. Chem.*, 1922, **124**, 185—202).—The volumetric methods of estimating sulphate are unsuitable on account of the filtrations involved. The authors have worked out the following method. Excess of barium nitrate is added to a sulphate solution, to this is added excess of potassium chromate and this excess estimated by running in a barium solution until the yellow colour disappears. Error by this method 0·3%. The use of silver salt as an indicator is not possible because the solubilities of silver and barium chromates are very near to one another. The following is given as a volumetric method of estimating lead; excess of chromate is added to a lead salt, a little silver nitrate is then added, and the excess of chromate is determined by titrating against a lead salt until the disappearance of the reddish-brown silver chromate. The latter method can also

be employed for the indirect estimation of sulphate. Titration of metals against arsenates and arsenites does not give positive results. The authors suggest the use of a copper solution as an indicator in acidimetry, the alkali being added until the precipitated hydroxide makes its appearance. W. T.

**Estimation of Selenium.** LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 464—466).—The method used for estimating sulphur (this vol., ii, 582, 656) may be employed also for the estimation of selenium if a larger excess of iron is taken and the exclusion of air during the reduction is rendered as complete as possible. By suitable modification of the procedure, sulphur and selenium may be estimated simultaneously (cf. *J. Soc. Chem. Ind.*, 1922, Dec.). T. H. P.

**Rapid Method for Estimating Ammonia in Ammonium Salts.** HERMANN BURKARDT (*Chem. Ztg.*, 1922, **46**, 949).—Attention is directed to a rapid method for estimating ammonia in its salts, in which formaldehyde solution (containing no free acid) is added to the solution containing an ammonium salt, and the acid formed according to the equation $6CH_2O+4NH_4Cl=6H_2O+4HCl+(CH_2)_6N_4$ is then directly titrated with a standard solution of sodium hydroxide, using phenolphthalein as an indicator. A. J. H.

**Titration of Nitrous Acid, and the Estimation of Nitrous and Arsenious Acids in the Presence of Each Other.** ALFONS KLEMENC (*Z. anal. Chem.*, 1922, **61**, 448—454).—The titration of acidified solutions of nitrites with permanganate in the air is attended with possible errors due to loss of nitrogen oxides and the slowness with which the reaction proceeds towards the end. These disadvantages may be overcome by adding the nitrite solution without acidifying to a solution containing an excess of potassium permanganate and sulphuric acid and enclosed in a glass-stoppered flask containing carbon dioxide under slightly reduced pressure. The solution is warmed at 40° to complete the reaction and the excess of permanganate is then titrated with standard oxalic acid.

[With F. POLLAK.]—The method is extended to the estimation of nitrous and arsenious acids in the same solution, one portion of which is titrated in the presence of sodium hydrogen carbonate with iodine for arsenious acid and another portion with permanganate as described above to obtain the sum of the two acids. Nitrous acid is then found by difference. A. R. P.

**The Use of Benzidine in the Detection of Phosphoric Acid.** F. FEIGL (*Z. anal. Chem.*, 1922, **61**, 454—457).—The yellow precipitate produced by ammonium molybdate in the usual test for phosphoric acid is often contaminated with arseno-molybdate and with molybdic acid, especially if an old solution of the reagent is used. To test this precipitate for the presence of phosphoric acid, it is collected on a close, ashless filter and washed somewhat, then moistened with a solution of benzidine hydrochloride containing acetic acid. The moist paper is held over an ammonia bottle, the vapour from which turns the precipitate blue in those parts con-

taining phosphoric acid. Even when no visible precipitate is produced in the test solution it should be poured through the paper and the paper tested as described. The blue colour is apparent when the original solution contains only 1 part of phosphorus as phosphoric acid in 460,000 parts of water. A. R. P.

**The Volumetric Estimation of Phosphoric Acid and of Sodium Phosphate and Pyrophosphates.** FRANK X. MOERK (*Amer. J. Pharm.*, 1922, **94**, 641—650).—Phosphoric acid and disodium hydrogen phosphate can be estimated volumetrically by titration with sodium hydroxide and hydrochloric acid, respectively, using a mixture of methyl-orange and indigo-carmine as indicator. To obtain results in consistent agreement with the silver phosphate precipitation method followed by titration of the liberated acid with alkali hydroxide until a permanent brown coloration of silver oxide is obtained, the dilution of the reacting solutions must be specified, and a definite quantity of sodium chloride must be added, the silver phosphate method being apparently unaffected by these factors. For the neutralisation method, using the indicator, the procedure is as follows. To 100 c.c. of water 0·2 c.c. each of 0·1% methyl-orange solution and 0·3% indigo-carmine solution are added, followed by dilute hydrochloric acid until the green colour changes without producing a violet colour. The solution thus prepared is divided into two equal parts, one being set aside and the other being added to the phosphoric acid or phosphate solution to be estimated, and the mixture titrated to match the tint of the reserved portion of the indicator solution with sodium hydroxide, or hydrochloric acid, as the case may be. The end-point corresponds in each case with the formation of $NaH_2PO_4$. Under these conditions and using $N/2$ solutions, results in agreement with the silver phosphate method were obtained by titrating in presence of 7·5% of sodium chloride for the phosphoric acid, and 2·5% for the phosphate. Under similar conditions, sodium pyrophosphate can be titrated with acid as a diacid base. G. F. M.

**Methyl-red in the Assay of Phosphoric Acid and Sodium Phosphate.** FRANK X. MOERK and EDWARD J. HUGHES (*Amer. J. Pharm.*, 1922, **94**, 650—655).—Of the two methods described in the preceding abstract and the U.S.P. IX method for the volumetric estimation of phosphoric acid and phosphates, the latter process always gives low results. The mixed indicator method is the most rapid, but is influenced by the weight taken, by the amount of sodium chloride present, and by the strength of the volumetric solutions. The best results when working with unknown quantities, are obtained by the silver phosphate method, titrating back the liberated acid with alkali hydroxide and using methyl-red as indicator. The procedure is as follows. To 50 c.c. of standard silver nitrate solution one drop of methyl-red and a trace of alkali to produce a yellow colour are added, followed by 10 c.c. of the solution to be assayed. The liberated nitric acid (3 mols. per mol. of $H_3PO_4$, or 1 mol. per mol. of $Na_2HPO_4$) is titrated with alkali hydroxide until the supernatant liquid is again yellow. During the neutralisation,

the pink colour may fade, in which case one or two drops more of methyl-red must be added. G. F. M.

**The Iodometric Micro-estimation of Phosphoric Acid, and of Phosphorus in Organic Compounds.** O. SVANBERG, K. SJÖBERG, and G. ZIMMERLUND (*Arkiv Kem. Min. Geol.*, 1922, No. 10, 1—17).—An improvement on Neumann's method (A., 1903, ii, 243; 1905, ii, 68) for the micro-estimation of phosphorus is described, in which the phosphorus is precipitated as ammonium phosphomolybdate, and the nitrogen in the precipitate estimated by Bang's micro-Kjeldahl method, in which the ammonia is absorbed in acid, the excess of the latter being estimated by adding excess of potassium iodide and potassium iodate and titrating the liberated iodine with thiosulphate. If a correction is made for a systematic error, 0·05—1·00 mg. of phosphorus may be estimated to within 2—3%. W. O. K.

**Titration of Boric Acid in Presence of Phosphoric Acid.** I. M. KOLTHOFF (*Chem. Weekblad*, 1922, **19**, 449—450).—Addition of sodium citrate to solutions containing phosphoric and boric acids prevents interference by the latter in the titration of the phosphoric acid with sodium hydroxide. After the neutralisation, addition of mannitol allows of the titration of the boric acid by further addition of sodium hydroxide, addition of the alkali being continued until the pink colour of the phenolphthalein remains for at least three minutes, and is not destroyed by further addition of mannitol. Neither calcium nor magnesium interfere.

In boiling solutions containing boric acid, a reflux condenser is scarcely necessary, since after half an hour's boiling the loss is less than 1%. S. I. L.

**The Estimation of Boric Acid.** W. W. DEERNS (*Chem. Weekblad*, 1922, **19**, 480—481).—The author's method of estimating boric acid in presence of phosphoric acid by means of potassium iodide–iodate is simpler than the method proposed by Kolthoff (preceding abstract) of adding sodium citrate and titrating with alkali, and the interference of calcium compounds is not apparent. The citrate method is not new, having been proposed by Littmann (*Chem. Ztg.*, 1898, **22**, 691) and Pfyl (A., 1914, ii, 290). S. I. L.

**Quantitative Estimation of Carbon and Hydrogen by means of the Sulpho-chromic Mixture.** L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1922, **175**, 525—527; cf. Guyot and Simon, A., 1920, i, 285, and ii, 332).—The method indicated is limited in scope, but is applicable to dibasic straight-chain acids, their methyl esters, and to all sugar derivatives which do not contain a methyl group directly linked to carbon, to aromatic acids, and to phenols which contain no alkyl substituents in the ring. The substance is completely oxidised by a known excess of reagent, the volume of carbon dioxide obtained is noted, and hydrogen estimated by determining volumetrically the excess of chromic acid. An alternative method depends on estimating the residual chromic

acid by addition of a known excess of a suitable organic substance and a second reading of the volume of carbon dioxide. A table is given of results obtained by the method as compared with standard figures for the same substances. The authors suggest that the method would be more generally applicable if silver chromate were used as the oxidising agent. H. J. E.

**The Function of Chromic Oxide in Oxidation by means of Sulpho-chromic Mixture.** L. J. Simon (*Compt. rend.*, 1922, **175**, 768—770; cf. preceding abstract).—Chromic oxide formed in the reaction may play an important part in the oxidation. Control experiments in which chrome alum was added to the reagent showed that, in absence of oxidisable organic matter, the addition enables the liberation of oxygen to take place more readily and that the quantity of alum added influences the amount of oxygen evolved. If sufficient chromic oxide is added, sulphuric acid will completely decompose chromic anhydride on heating at 100°. Thus the addition of chromic oxide or its derivatives, when dealing with organic substances which are only partly oxidised by sulpho-chromic mixture, transforms what would otherwise be partial into complete oxidation, and in extreme cases gives rise to the evolution of free oxygen.
H. J. E.

**The Tannic Acid Method for the Estimation of Carbon Monoxide in Blood.** R. R. Sayers and W. P. Yant (*U.S. Bur. Mines, Rep. Investigations*, 1922, No. 2356).—Standards are prepared containing 10—100% of carbon monoxide-hæmoglobin in 90—0% of oxyhæmoglobin as follows: 5 c.c. or more of blood are collected, 0·05 gram of potassium citrate or 0·02 gram of sodium fluoride being used for each 10 c.c. Half of the blood is saturated with carbon monoxide, and both parts are diluted to 10 vols. with water, and mixed in varying proportions. Then 0·1 c.c. of the blood to be tested is drawn from the finger into 1 c.c. of 0·05% potassium citrate or 0·03% sodium fluoride solution. To each of the blood samples contained in tubes of $\frac{5}{16}$ inch inside diameter is added 1 c.c. of 1% tannic acid in 1% pyrogallol solution. The tubes are inverted and comparison is made in eight to ten minutes. The standards, when properly sealed, may be kept for several weeks, but the reagent should be freshly prepared. Chemical Abstracts.

**Physical Method for the Estimation of Carbon Dioxide in the Respiratory Air.** A. K. Noyons (*Arch. Néerland. physiol.*, 1922, **7**, 488—495).—A method is described for the estimation of carbon dioxide by the measurement of the heat conductivity of the mixture of gases. W. O. K.

**Estimation of Silica in Filtered Sea-water.** Roger C. Wells (*J. Amer. Chem. Soc.*, 1922, **44**, 2187—2193).—The author has investigated the estimation of silica in sea-water and finds that the most effective method is to add an aluminium salt if such is not already present and precipitate with a quantity of ammonia sufficient to produce a pink colour with rosolic acid; the silica carried down with the alumina is then recovered and estimated in

the usual way. It is shown that silica cannot be estimated by the loss on evaporation with hydrofluoric acid in the presence of calcium sulphate. An excess of at least two parts of alumina to one of silica is essential for the complete inclusion of silica in the alumina precipitate. An excess of ammonia favours the inclusion of silica in the ammonia precipitate, but this has a slightly solvent action on the aluminium hydroxide. A Sörensen value of 7—8, as shown by the pink colour with rosolic acid, is advisable in making the ammonia precipitation. A very small quantity of silica, roughly 0·3 mg., escapes precipitation and an equal quantity is generally found in the wash waters from the ammonia precipitate. In rock analysis, a single evaporation with hydrochloric acid is sufficient, provided silica is also determined in the ammonia precipitate. Eleven samples of water collected one mile south of Eastern Point Light, Gloucester, Mass., during eleven months gave contents of dissolved silica varying between 0·0029 and 0·0003 gram per litre. J. F. S.

**The Estimation of Alkali Carbonates in Presence of Phenolphthalein.** BONNIER (*Compt. rend.*, 1922, **175**, 765—767).—Warder's method (A., 1881, 848) of estimating carbon in steel involves a titration of alkali hydroxide with sulphuric acid in presence of alkali carbonate. That of Winkler (Treadwell, "Analytische Chemie," 9th ed., **2**, 485) necessitates titration of the hydroxide in presence of barium chloride. Neither gives a sharp end-point. In the former case, the instability of the alkali hydrogen carbonate, on the formation of which the end-point depends, leads to errors and a study of the various factors which influence the result shows that the excess of sodium sulphate formed, the temperature, and the method of stirring have no effect. The initial colour of the indicator, the method of adding the acid, and the dilution (cf. Mestrezat, A., 1918, ii, 274) all affect the estimation to some extent. Winkler's method is satisfactory if carried out with normal solutions; with less concentrated solutions, however, the end-point tends to lose sharpness. H. J. E.

**The Cobalt Nitrite Reaction for Potassium in Animal and Vegetable Cells.** A. B. MACALLUM (*Arch. Néerland. physiol.*, 1922, **7**, 304—308).—Sodium cobaltinitrite is a very sensitive reagent for the microchemical detection of potassium in animal and vegetable cells. The possibility of ammonia being precipitated by the cobaltinitrite may be avoided by the addition of formalin to the reagent, which converts the ammonia into hexamethylenetetra-amine. The only difficulty in the use of the reagent is that in animal tissue creatine may give a precipitate likely to be mistaken for potassium. W. O. K.

**The Volumetric Estimation of Calcium.** A. VÜRTHEIM and G. H. C. VAN BERS (*Chem. Weekblad*, 1922, **19**, 450—452).—Excess of ammonium oxalate is added to the solution, and after heating to boiling, calcium oxalate is precipitated by addition of ammonia; after filtration, the excess of ammonium oxalate is titrated with permanganate in the usual way. It is necessary to

use at least double the amount of oxalate theoretically required for the precipitation; on account of the rapid alteration of ammonium oxalate solutions, blank titrations must be carried out with each series of estimations.

*The results agree very well with those obtained by the gravimetric* estimation, and within very wide limits are independent of the temperature and degree of acidity of the solution to be titrated and of the strength of the permanganate solution employed.

S. I. L.

**The Volumetric Estimation of Magnesium in Potassium Salts.** A. VÜRTHEIM (*Chem. Weekblad*, 1922, **19**, 461—462).—The method proposed by Precht (A., 1879, 1053), namely precitation of magnesia by addition of carbonate-free alkali, and back titration of the excess after filtration, has been examined, and found to give satisfactory results for mixtures containing very large quantities of sodium, potassium, and calcium salts. Where calcium is present, oxalate is added to the alkali to ensure complete precipitation. S. I. L.

**Estimation of Lead in Lead Amalgam.** M. G. MELLON (*J. Amer. Chem. Soc.*, 1922, **44**, 2167—2174).—A résumé is given of the principles of the methods which have been used previously for the estimation of lead in lead amalgams. Data are presented which show the possibility of estimating quantities of lead of about 0·5 gram of lead in 30—50 grams of mercury with an accuracy of 0·05%. The method consists in the displacement of the lead by copper from an aqueous solution of copper nitrate, followed by the precipitation of the lead as chromate from the solution. It is shown that 0·4 gram of lead may be displaced from the amalgam in thirty minutes at the ordinary temperature if the mixture is stirred, but if allowed to remain stationary many hours are required for complete precipitation. The following procedure is recommended: the sample of amalgam is covered with water containing one drop of 10% acetic acid, 10 c.c. of a 2*N*-solution of copper nitrate are added and the mixture is stirred for thirty minutes and filtered to remove any metallic copper which has not dissolved in the mercury. One drop of 10% acetic acid is added to the filtrate, and the lead is precipitated as chromate by the method usually adopted. J. F. S.

**A Peculiar Catalytic Reaction for the Detection, and a Method for the Estimation, of the Smallest Traces of Copper [also a Lecture Experiment].** FRIEDRICH L. HAHN and G. LEIMBACH (*Ber.*, 1922, **55**, [*B*], 3070—3074).—When a solution of a ferric salt is added to a solution of sodium thiosulphate a dark violet coloration is developed which gradually disappears as the ferric becomes reduced to ferrous salt and the sodium thiosulphate is converted into tetrathionate. The reaction is greatly accelerated by the presence of copper salts and its completion can be made more obvious by the addition of ammonium thiocyanate to the mixture; the latter substance has also the advantage of retarding the reaction.

The following solutions are required. Copper sulphate solution (3·9 grams of the hydrated salt per litre, of which 1 c.c. is diluted to 1 litre before use); ferric solution (5 grams of iron alum and 25 c.c. of $2N$-hydrochloric acid per litre); $5M$-ammonium thiocyanate solution; $1/15M$-sodium thiosulphate solution. For the recognition of the minutest traces of copper, two litres of the iron solution should be mixed with 10—20 c.c. of thiocyanate; for the estimation of larger amounts more thiocyanate (up to 200 c.c.) may be used.

A neutral solution of the substance under investigation is placed in a beaker (500 c.c. capacity) and in a similar series of beakers known quantities of copper solution are placed. The solutions are made up to a fixed volume with distilled water, and to each are added 100 c.c. of the iron thiocyanate solution. Simultaneously (by means of a row of test-tubes fastened to a rod which can be rotated horizontally) 25 c.c. of thiosulphate solution are added to each beaker and the contents well mixed. The times required for decolorisation (which are conveniently 10—20 minutes) are then compared.

The velocity of the reaction is rather greatly dependent on small variations in the ratio of the concentrations, iron : thiocyanate : thiosulphate, on the degree of acidity and the temperature, so that it is scarcely possible at present to indicate definite intervals of time for definite quantities of copper. It is necessary to observe the progressive decolorisation in the solution under investigation and in solutions of known copper content simultaneously and to use a sufficient volume of solution (about 100 c.c.) to avoid the effect of local variations of temperature. The smallest amount of copper which can be identified with certainty under these conditions is 0·002 m.g.; further refinement is probable if a thermostat is used.

A similar effect on the course of the reaction has not been observed with any other substance yet investigated. Acceleration is caused by relatively large amounts of platinum, but the effect is so little marked that a confusion with copper is impossible. Aluminium, zinc, nickel, and arsenic in particular retard the action, especially in strongly acid solution. If such metals are to be investigated with regard to their copper content, it is essential that an equal weight of "foreign" metal should he added to the control solutions; in this manner, 0·001% of copper in nickel can be rapidly and certainly detected. H. W.

**Potentiometric Titration of Copper.** E. Zintl and H. Wattenberg (*Ber.*, 1922, **55**, [*B*], 3366—3370).—The method consists in the reduction of the cupric to cuprous salt in hydrochloric acid solution by means of titanium trichloride and subsequent re-oxidation with standard potassium bromate or dichromate solution in an atmosphere of carbon dioxide.

The apparatus consists of a beaker placed on an electrically heated hot plate and covered with a clock glass provided with four holes for the introduction of the nozzle of the burette, a stirrer, a T-tube which holds the indicator electrode (a stout smooth platinum

wire) and serves also for the introduction of carbon dioxide and the limb of the normal electrode (a calomel cell charged with solid potassium chloride and saturated potassium chloride solution). The *E.M.F.* of the titration cell is measured by compensation in the usual manner with the aid of a capillary electrometer. The *copper solution is treated with a sufficient quantity of hydrochloric* acid and reduced by a slight excess of titanium trichloride, whereby a colourless solution resnlts if sufficient hydrochloric acid is present to prevent precipitation of cuprous chloride. The addition of standard bromate or dichromate solutiou causes the oxidation of the excess of tervalent titanium and subsequently that of the copper, the end-points of the two actions being marked by abrupt changes in the potential. Titration is effected at about 80°, at which temperature the potentials adjust themselves almost instantaneously; in cold solution, the bromate in particular reacts somewhat slowly with titanium trichloride. The concentration of the hydrochloric acid has not a very marked influence, and is suitably maintained at 4—8%. Considerable quantities of ammonium salts have no disturbing effect, but iron is titrated with the copper. Small quantities of nitric acid are reduced by the excess of titanium trichloride, after which they do not influence the change further. The use of stannous chloride in place of titanium chloride is not recommended, since the potentials, even in hot solution, only become constant slowly as long as an excess of stannous salt is present. H. W.

**Volumetric Estimation of Copper by means of Sodium Nitroprusside.** GEORGES JORET (*Ann. Falsif.*, 1922, **15**, 354—356).—A solution of the copper salt, containing about 0·1 gram of copper, is neutralised with ammonia, then acidified slightly with nitric acid, treated with 40 c.c. of *N*/10-sodium nitroprusside solution (14·895 grams per litre), diluted to 200 c.c., and filtered; 100 c.c. of the filtrate are treated with 20 c.c. of *N*/10-silver nitrate solution, the mixture is filtered, and the excess of silver nitrate titrated with *N*/10-thiocyanate solution in an aliquot portion of the filtrate. The copper solution must not contain silver, nickel, cobalt, or halogens. W. P. S.

**Separation of Copper by means of Thiophenylhydantoic Acid.** H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2253—2254).—In solutions slightly acidified with acetic acid, thiophenylhydantoic acid precipitates quantitatively copper, lead, mercury, cadmium, bismuth, and antimony, whilst arsenic, tin, and metals not precipitated by hydrogen sulphide are not precipitated under these conditions. When the copper precipitate is ignited to oxide, the product contains sulphate sufficient to cause an error of 0·1—0·6 mg. in the total weight. The copper compound is very unstable and quite unsuitable for direct weighing. To estimate copper by means of the precipitate with thiophenylhydantoic acid, it is best to fuse it with potassium pyrosulphate, dissolve in water, and estimate the copper by any of the well-known methods. The bismuth and antimony compounds

ith thiophenylhydantoic acid are soluble in alcohol. To separate )pper from the metals of the iron and zinc groups, the solution is ɜutralised with ammonia and 5 grams of glacial acetic acid are ldded. If metals precipitated by ammonia are present, 7 grams of tric acid are added before neutralising for every gram of such .etal present. The solution is made up to 300—400 c.c., raised to ıe boiling point, and treated with 0·5 gram of thiophenylhydantoic ;id in a little hot water, then dilute ammonia is added until a ɜllow precipitate begins to form. The solution is boiled, and all the copper is precipitated the precipitate separates at the ›p, leaving a clear solution below. If this does not happen, a ;tle more ammonia is added, but this may cause the precipitate ı turn brown, due to the formation of sulphide. The precipitate filtered hot, washed with hot water, and treated as stated above. he method is very good for small quantities of copper.

J. F. S.

**Contradictions and Errors in Analytical Chemistry. I. he Precipitation of Aluminium by Thiosulphate and its eparation from Iron. II. The Ageing of Volumetric hiosulphate Solutions.** FRIEDRICH L. HAHN [with G. LEIM-ACH (I) and H. WINDISCH (II)] (*Ber.*, 1922, **55**, [*B*], 3161—3165).—The precipitation of aluminium by means of thiosulphate under ıe usual conditions (boiling the solution until sulphur dioxide is ›mpletely expelled and then adding ammonia) is only very complete; the apparent accuracy of the results is due to a balance errors, the unprecipitated aluminium hydroxide being com-ɜnsated by the alkali carried down by the precipitate. Pre-pitation is almost quantitative when the solution is boiled for ıly a short time and the remainder of the metal is precipitated y addition of a base. An almost complete separation from iron ın be achieved if a very weak base, preferably phenylhydrazine, used.

II. The addition of a very small amount of alkali enables thio-ılphate solutions to be preserved without alteration in strength om the first day. The change which they otherwise suffer appears ı be caused by the faintly acid reaction of distilled water; it ɜrtainly does not depend on the formation of sulphite or sulphide.

H. W.

**The Separation of Ferric Oxide and Aluminium Oxide om Magnesium Oxide by the Nitrate Method.** ANDRÉ HARRIOU (*Compt. rend.*, 1922, **175**, 693—695; cf. this vol., 319).—In separating the oxides of iron and aluminium from that magnesium by heating with ammonium nitrate, the retention of agnesium oxide by the other oxides increases with the magnesium ›ntent; aluminium oxide retains a relatively smaller amount than rric oxide. By increasing the concentration of the ammonium trate solution from 4% to 10%, the magnesium oxide is almost ›mpletely removed, and if the mixture is treated three times in is way, no trace of magnesium remains. H. J. E.

**Separation and Estimation of Cobalt. I. Separation of Cobalt by means of Thiophenylhydantoic Acid. I. Separation of Cobalt from other Metals.** H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2219—2226).—Cobalt may be quantitatively separated from arsenic, uranium, vanadium, titanium, tungsten, molybdenum, zinc, manganese, chromium, aluminium, magnesium, and calcium by precipitation with thiophenylhydantoic acid in slightly ammoniacal solution. In the presence of iron, the precipitate is rarely free from this impurity, and usually contains from one to five mg. regardless of the amount originally present. This does not, however, interfere with the volumetric estimation of cobalt. Nickel is always partly precipitated. The cobalt precipitate has not a definite composition, and is probably mixed with some cobalt sulphide, thus making it necessary to convert the cobalt into some other more definite form. The various separations of cobalt from other metals are effected as follows. *Separation from iron.* A solution containing 1 gram of iron and 25 mg. of cobalt in 300 c.c. is placed in an Erlenmeyer flask, treated with 8 grams of citric acid, and neutralised with ammonia (*d* 0·90) and 5 c.c. of excess ammonia are added. The solution is warmed at 35°, 0·7—1·0 gram of thiophenylhydantoic acid dissolved in 30 c.c. of water or alcohol added and the mixture shaken vigorously for several minutes. The cobalt is precipitated and after boiling the precipitate may be easily filtered. *Separation from manganese.* This separation is effected as in the case of iron. *Separation from zinc.* The procedure is the same as for iron, except that an excess of 10 c.c. of ammonia is necessary and the solution must be boiled for several minutes to ensure complete precipitation of the cobalt. The other metals named are separated in the same way as zinc, except that 7 grams of citric acid are used. J. F. S.

**Separation and Estimation of Cobalt. II. Gravimetric Estimation of Cobalt.** H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2226—2231; cf. preceding abstract) —Various methods for the gravimetric estimation of cobalt have been examined, and it is shown that, although pure cobalt nitrate may be accurately ignited to the oxide $Co_3O_4$ and the latter reduced by hydrogen to the metal, the oxide obtained by the ignition of the thiophenylhydantoic acid precipitate (*vide supra*) contains a little sulphate. If the oxide obtained in this ignition is assumed empirically, to be $Co_2O_3$, the results for cobalt are fairly good. The ignition of cobalt sulphate at 550° is the most accurate method for the estimation of cobalt, but when this method is applied to the thiophenylhydantoic acid precipitate the results are usually slightly high and the sulphate is not completely soluble in water. The electrolytic estimation of cobalt is very satisfactory when the proper conditions and precautions are observed. Precipitation as cobalt ammonium phosphate followed by ignition to cobalt pyrophosphate is less accurate than the preceding methods.

**Separation and Estimation of Cobalt. III. Volumetric Estimation of Cobalt.** H. H. Willard and Dorothy Hall (*J. Amer. Chem. Soc.*, 1922, **44**, 2237—2253; cf. preceding abstracts).—A number of methods have been examined for the volumetric estimation of cobalt. It is shown that in general volumetric methods are the most accurate and satisfactory for the estimation of cobalt. The most accurate method involves the oxidation of cobalt to cobaltic hydroxide in strongly alkaline solution by means of a perborate or hydrogen peroxide, followed by its volumetric reduction to a cobaltous salt. This reduction may be accomplished by the following methods: (*a*) By the addition of potassium iodide in acid solution, the iodine liberated being titrated with sodium thiosulphate; in this method iron must be absent. (*b*) By adding the cobaltic hydroxide to an acid ferrous sulphate solution, the excess of which is titrated with potassium permanganate; an empirical factor must be used in the calculation. (*c*) By the addition of a strongly acid solution of stannous chloride, the excess of which is titrated with iodine, iodate, bromate, or dichromate solution. The last, titrated electrometrically, is especially recommended. If iron is present, iodine will oxidise it quantitatively only in a neutral solution. (*d*) By adding titanous sulphate, the excess of which is titrated with permanganate. Since titanous hydroxide decomposes water with the liberation of hydrogen, the alkaline solution must be first almost completely neutralised by one of the several methods suggested. The presence of nickel does not interfere with this titration, but the oxidation is incomplete when more than 7 mg. of iron are present. In the presence of a large excess of potassium hydrogen carbonate, cobalt is oxidised by hydrogen peroxide to a green tervalent compound, which is reduced in the presence of pyrophosphate by ferrous sulphate, the excess of which is titrated with permanganate after acidifying with sulphuric acid. Iron and manganese in small amounts do not interfere in this method, but the principal source of error is in the removal of the excess of peroxide without decomposing the cobalt compound. J. F. S.

**Gravimetric Estimation of Nickel as Nickel Dioxide.** Wilhelm Vaubel (*Chem. Ztg.*, 1922, **46**, 978).—Nickelous hydroxide is precipitated from the solution with sodium hydroxide, collected, washed, and ignited. The ignited precipitate is again washed until free from alkali metals, dried, and dissolved in nitric acid. The excess of nitric acid is evaporated and the residue heated for thirty minutes in an air-bath at 280—330°. Pure black nickel dioxide results. The oxides of nickel at present known are NiO, $Ni_3O_4$, and $NiO_2$. The oxide $Ni_2O_3$ has not yet been obtained. H. C. R.

**Electrometric Estimation of Nickel with Silver Nitrate.** Erich Müller and Hans Lauterbach (*Z. anal. Chem.*, 1922, **61**, 457—464).—The nickel solution is treated with a slight excess of potassium cyanide solution, sufficient to decolorise the mixture, and connected with a normal calomel electrode, a galvanometer

and a sliding resistance, the ends of which are connected with an accumulator, and one end and the sliding contact with a voltmeter. A silver wire in the solution acts as indicator electrode, and the solution is agitated by means of a motor-driven stirrer. The sliding resistance is adjusted until the voltmeter indicates 0·075 volt and silver nitrate solution is added slowly until the galvanometer indicates zero. The results are calculated as in the older chemical process. A. R. P.

**Electrometric Titration of Dichromate with Ferrous Sulphate.** Marion Eppley and Warren C. Vosburgh (*J. Amer. Chem. Soc.*, 1922, **44**, 2148—2156).—The conditions under which dichromate may be estimated by electrometric titration with ferrous sulphate have been investigated. The practical limits of acidity for hydrochloric and sulphuric acids have been determined. It is shown that the amount of ferrous sulphate required to titrate a given amount of chromic acid varies with the concentration of the latter. Dissolved air has a negligible effect on the titration. Hydrofluoric acid in sufficient concentration reduces the amount of ferrous sulphate required by about 0·1%. When ferrous sulphate, standardised by means of a standard solution of potassium permanganate, is used to standardise a known amount of dichromate in 0·01*N*-solution, the value found for the latter is about four parts per thousand higher than the calculated value. When the dichromate concentration is 0·003*N*, the amount of ferrous sulphate required is about 1% higher than the calculated quantity. The titration of the ferrous ion with a potassium dichromate solution gives results which agree with those obtained by the reverse titration. J. F. S.

**The Analysis of High-percentage Tungsten Alloys.** K. Seel (*Z. angew. Chem.*, 1922, **35**, 643—644).—The serious loss of platinum involved in the customary fusions of tungsten alloys with sodium and potassium carbonates and nitrates may be avoided by fusing the finely divided alloy with sodium hydroxide and nitrate in silver crucibles. The fusion takes about 1 hour, and the crucibles are not seriously attacked. 0·5 Gram of the finely divided alloy is fused with 6 grams of sodium hydroxide and 3 grams of sodium nitrate. The fused mass is dissolved in water and filtered, the iron oxide remaining on the filter being dissolved in hydrochloric acid containing a little potassium chlorate, filtered, and the two filtrates united. The iron is estimated as ferric oxide as usual. The aluminium and the greater part of the silica are removed from the filtrate with ammonia, filtered off, and the tungsten in the filtrate precipitated with mercurous nitrate after acidifying, boiling off the carbon dioxide and concentrating to about 150 c.c. The tungstic acid obtained by ignition of the precipitate is strongly contaminated with alkali, which is removed by repeated extractions with 7% hydrochloric acid, and traces of silica are finally removed by treatment with hydrofluoric acid. In the case of alloys rich in iron, a residue containing iron and tungsten remains after the original fusion. This is fused with pyrosulphate and the tungsten

precipitated with nitric acid, estimated as tungstic acid and added to the figure obtained above. The iron in the filtrate is estimated in the usual way and added to the figure obtained above.

H. C. R.

**Separation of Antimony from Arsenic and Tin.** FRIEDRICH L. HAHN (*Z. anorg. Chem.*, 1922, **123**, 276).—Antimony can be separated quantitatively from arsenic and tin by oxidation to pyroantimonate (cf. A., 1916, ii, 266). This method is due to Hampe. W. T.

**The Estimation of Bismuth as Metal.** ALBIN KURTENACKER and FELICITAS WERNER (*Z. anorg. Chem.*, 1922, **123**, 166—170).—The authors find that metallic bismuth can be accurately *estimated by dissolving it in a ferric salt and titrating the ferrous* salt produced by means of potassium permanganate, the reaction being $Bi+3Fe^{\cdot\cdot\cdot}=Bi^{\cdot\cdot\cdot}+3Fe^{\cdot\cdot}$. Ferric chloride was found more suitable than the sulphate. The reduction of bismuth nitrate by formaldehyde, hypophosphorous acid, and alkali stannite gave results about 5% too low, this being due to the metal being mixed with some bismuthous oxide. Conditions for complete reduction to the metal could not be found. W. T.

**New Method for Estimating Volatile Substances in Air.** E. FRITZMAN and K. MACJULEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 212—226).—To estimate the content of light petroleum vapour in air, the latter is first freed from dust, moisture, and carbon dioxide by passing it through tubes containing, in order, soda-lime, calcium chloride, phosphoric oxide, and cotton wool, the light petroleum being retained in two **U**-tubes packed with magnesium turnings and cooled in liquid air. T. H. P.

**Estimation of Toluene, Xylene, and Benzene.** G. ZABOROWSKI (*Mat. grasses*, 1922, **14**, 6160—6161).—Commercial samples of the above hydrocarbons or their respective mixtures with "gasoline" may be examined, either volumetrically by sulphonation *with a known quantity of sulphuric acid and titration* of the excess of acid, or densimetrically. (*a*) About 3·5 grams of the sample and three times its weight (for xylene, four times) of (preferably 100%) sulphuric acid are warmed to 45° in a 50 c.c. glass-stoppered flask, shaken thoroughly for five minutes, allowed to cool, poured into 100 c.c. of water, boiled to remove light oils, and titrated with standard sodium hydroxide solution, using phenolphthalein. For toluene, the quantity of acid used is multiplied by 1·876; for xylene, by 2·163. In the case of benzene, sulphonation must be effected in a reflux apparatus. (*b*) The densimetric estimation consists in the use of the expression $T=-[100D(d_1-d_2)]/(D-d_2)d_1$, where $d_1$ represents the $d_{15}$ of the sample, $d_2$ the $d^{15}$ of the unsulphonated residue after sulphonation, and $D$ the $d^{15}$ of pure toluene (0·8706), xylene, or benzene. CHEMICAL ABSTRACTS.

**The Detection of Nitro-compounds.** H. J. PRINS (*Perf. Essent. Oil Rec.* 1922, **13**, 355).—The accelerating effect of nitro-

benzene on the reaction velocity of metals with weak acids is applied to the detection of this substance in benzaldehyde. The reaction is carried out by heating 2 c.c. of the oil and 6 c.c. of 80% acetic acid for one minute with a small piece of tin foil. In presence of 5% of nitrobenzene, the tin disappears immediately on boiling, with 1% the tin turns dark and disappears about ten minutes after the mixture has been heated, with 0·1% the tin turns black after about ten minutes, with 0·01% the tin becomes greyish-black after remaining over-night, whilst with pure benzaldehyde the metal retains its bright surface. In a similar way, the presence of 0·1% of artificial musk can be detected in perfumes. The reaction is not exclusively specific for nitro-compounds, as organic peroxides have the same property, but only oils rich in terpenes which contained peroxides owing to exposure to air show the reaction and then only feebly. Likewise worm-seed oil containing the peroxide caridol can scarcely give rise to confusion, as 5% of nitrobenzene in benzaldehyde reacts more rapidly than pure worm-seed oil. Peroxidised benzaldehyde does not show the nitrobenzene reaction at all. G. F. M.

**Estimation of Phenol in Mixtures of Tar Acids.** W. H. Hoffert (*J. Soc. Chem. Ind.*, 1922, **41**, 334—337T).—The method proposed depends on the fact that the freezing point of phenol hydrate (16°) is lowered to the same extent by equal weights of each of the three cresols. In the case of a mixture of phenol and cresols, the freezing point may be determined directly, after the addition of water amounting to 10% of the weight of the mixture, if the quantity of phenol present exceeds 55%; if the proportion of phenol is less, a known quantity of pure phenol (m. p. 40·5°) must be added to bring the proportion above 55%. With a mixture of tar acids, it is first necessary to remove neutral hydrocarbons and pyridine bases by distilling with steam from a sodium hydroxide solution of the sample, or by extracting the same solution with ether or benzene; the recovered tar acids are then distilled. If the mixture distils completely below 203°, the estimation is made directly on the distillate, but otherwise, higher homologues must be separated by fractional distillation. A known weight of pure phenol is added to the distillate and the mixture is treated with 10% of its weight of water. Directions are given in detail regarding the procedure adopted for determining the freezing point and the amount of phenol corresponding with the freezing point obtained is found by reference to a graph. The method may be applied to the estimation of phenol in crude carbolic acid. W. P. S.

**Iodometric Estimation of Sugars.** Fr. Auerbach and E. Bodländer (*Z. angew. Chem.*, 1922, **35**, 631—632).—In the iodometric titration of the excess of Fehling's solution used in the estimation of a reducing sugar, the volume of $N/10$-thiosulphate solution required is not strictly proportional to the amount of sugar present. A table is given showing the quantities of invert-sugar corresponding with different quantities of thiosulphate

solution. Replacement of a part of the potassium iodide used by potassium thiocyanate, as proposed by Bruhns, is not recommended.
W. P. S.

**The Modified Lehmann Method for the Estimation of Dextrose. Adaptation to Small Quantities of Reducing Sugars.** PAUL FLEURY and LOUIS BOUTOT (*Bull. Soc. Chim. Biol.*, 1922, **4**, 361—374).—In the estimation of dextrose by Bruhns's method (A., 1920, ii, 773) the reagents should be added to the copper solution in the following order: iodide, acid, thiocyanate. The method has been used for the estimation of small quantities of reducing sugars in biological fluids. E. S.

**Trustworthiness of the Benedict and Folin-Wu Blood-sugar Estimations.** F. A. CSONKA and GRACE C. TAGGART (*J. Biol. Chem.*, 1922, **54**, 1—3).—The different results obtained by the Folin-Wu (A., 1920, ii, 337) and the Benedict (A., 1918, ii, 247) methods are due to the presence in blood of a substance which reacts with picric acid but does not reduce copper solutions. The former method is thus the more trustworthy. E. S.

**Estimation of Starch. I. Estimation of Starch in Barley and in Wheat.** ARTHUR R. LING [with E. H. CALLOW and W. J. PRICE] (*J. Inst. Brewing*, 1922, **28**, 838—853).—The method proposed depends on the hydrolysis of the starch by malt diastase as suggested by Brown and Morris (T., 1885, **47**, 527). Since the amount of maltose yielded by a pure starch varies with the diastatic power of the malt, the authors have determined the relation between the percentage of maltose obtained from pure barley and wheat starches when these are hydrolysed under definite conditions, and the diastatic power of the malt employed. The results of these experiments are given in graphic form. To estimate starch in barley or wheat, 5 grams of the finely-powdered grain are extracted in a Soxhlet apparatus for 3—3½ hours with alcohol (*d* 0·920), the powder is then rinsed into a beaker with about 100 c.c. of water, and the mixture is boiled for ten minutes. The starch paste thus obtained is cooled to 57°, 10 c.c. of malt extract (prepared from a malt of known diastatic power) are added, the mixture is kept at 57° for one hour, then boiled, filtered, and the insoluble portion washed. The filtrate is diluted to 200 c.c. and 30 c.c. of this solution are diluted to 100 c.c. and titrated against 10 c.c. of Fehling's solution. The cupric reducing power of the malt extract is determined at the same time and under the samo conditions, and the value obtained is used to correct the reducing power of the conversion product. W. P. S.

**Identification of Inulin by a Mycological Method.** ALDO CASTELLANI and FRANK E. TAYLOR (*Biochem. J.*, 1922, **16**, 655—658).—*Monilia macedoniensis*, Castellani, ferments inulin with the production of gas. It also ferments dextrose, lævulose, galactose, and sucrose. The method consists of the utilisation of the above mould in conjunction with other fungi. S. S. Z.

**Estimation of Volatile Acids in Wine.** PHILIPPE MALVEZIN (*Ann. Falsif.*, 1922, **15**, 360—362).—In reply to criticism, the author states that he sees no reason for altering the procedure described in his ether-extraction method for the estimation of volatile acids in wine. Tartaric and lactic acids are not extracted by the ether under the conditions given. W. P. S.

**The Separation of Solid and Liquid Fatty Acids.** W. MEIGEN and A. NEUBERGER (*Chem. Umschau*, 1922, **29**, 337—342).—The methods of Varrentrapp, Bull and Fjellanger, Farnsteiner, David, Niegemann, and Facchini and Dorta were tested on known mixtures of solid and liquid fatty acids and by none was a true quantitative separation obtained. By the methods of Bull and Fjellanger, Facchini and Dorta, and David about one-half of the liquid acids was recovered in a nearly pure state. By recrystallising the solid fraction, part of this was also obtained nearly pure. By precipitating the aqueous solution of the potassium salts with excess of thallous sulphate, however, an almost quantitative separation of stearic, palmitic, and elaidic acids from oleic acid was attained, and no recrystallisation was necessary. A mixture of 0·502 gram of oleic acid with 0·505 gram of stearic acid gave 0·509 gram of solid acids of iodine value 0·3 and m. p. 68°, whilst a mixture of 0·200 gram of oleic acid and 0·502 gram of stearic acid gave 0·529 gram of solid acids of iodine value 0·9 and m. p. 67·5°. H. C. R.

**The Neutralisation of Tartaric Acid by Potassium Hydroxide in Presence of Chlorides of Alkaline Earths.** L. J. SIMON and L. ZIVY (*Compt. rend.*, 1922, **175**, 620—622).—The fact that titration of alkali hydroxide against tartaric acid gives two end-points; that with helianthin indicating formation of the acid salt and that with phenolphthalein the normal salt, may be used in estimating mixtures of tartaric acid with other acids which give an end-point in presence of helianthin indicating the formation of normal salt. The presence of alkaline-earth chlorides in the solution introduces an error, as each molecule behaves towards potassium hydroxide as an equivalent quantity of hydrochloric acid. This effect is produced by any quantity and is quantitative in each case, the limiting value of the effect being the amount of tartaric acid present. Chlorides of other metals do not interfere with the titration in this manner. H. J. E.

**Estimation of Salicylic Acid in Blood-serum and other Fluids of the Body.** H. HERISSEY (*Compt. rend. Soc. biol.*, 1922, **87**, 333—336).—A mixture of 10 c.c. of serum, 5 c.c. of water, 0·5 c.c. of a solution of 1 gram of sulphuric acid in 5 c.c. of water, and 40 c.c. of ether is shaken together for one minute in a stoppered glass bottle of 125 c.c. capacity. After an interval of a few minutes, 4·5 c.c. of sulphuric acid solution are again added and the contents well mixed by rotation of the flask, the supernatant ethereal layer

being decanted after five minutes. Of this solution, 30 c.c. are shaken in a funnel with 2—3 grams of anhydrous sodium sulphate; 3 c.c. of water containing one drop of dilute ferric chloride solution are then added, and the whole is vigorously shaken. In the presence of salicylic acid, a violet colour appears in the water layer on keeping. Should a positive reaction be given, the contents are thoroughly mixed and transferred to a small crystallising dish, the ether being allowed to evaporate spontaneously at room temperature. It is necessary to use a stirring-rod to prevent the formation of deposits on the sides of the dish. The solution is then filtered into a test-tube, together with a few drops of rinsing water, and its coloration compared with standards prepared from 10 c.c. of normal serum, 5 c.c. of water, and varying quantities of salicylic acid. A definite coloration is obtained with only 10 mg. of sodium salicylate per litre. CHEMICAL ABSTRACTS.

**Substituted Naphthalenesulphonic Acids. I. A Method for Identifying H-Acid and its Intermediates Obtained from Naphthalene-2 : 7-disulphonic Acid.** D. F. J. LYNCH (*J. Ind. Eng. Chem.*, 1922, **14**, 964—965).—A method for the detection of 1 : 8-dinitronaphthalene-3 : 6-disulphonic, 1 : 8-diaminonaphthalene-3 : 6-disulphonic, 1-amino-8-naphthol-3 : 6-disulphonic (H-acid), and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic (chromotropic) acids in their mixtures by means of their reactions with solutions containing 2-cymidine sulphate, cobalt chloride, zinc sulphate, or the hydrochlorides of benzidine, α-naphthylamine, ψ-cumidine, tolidine, and *p*-nitrotoluidine, is developed. The tests are carried out with 3—5 c.c. of less than one-tenth gram-molecular solutions of the naphthalenesulphonic acids. The following substances were prepared. *Benzidine* salt of 1 : 8-*dinitronaphthalene*-3 : 6-*disulphonic acid*,

$$C_{10}H_4(NO_2)_2(SO_3H)_2,NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2,$$

light yellow prisms, m. p. 275° (decomp.). Solubility 0·036 part at 20°. *Cymidine* 1 : 8-*dinitronaphthalene*-3 : 6-*disulphonate*, $C_{10}H_4(NO_2)_2(SO_3H)_2,(C_6H_3MePr^{\beta}\cdot NH_2)_2$, straw-coloured prisms, m.p. 265° (decomp.), solubility 0·059. Benzidine salt of chromotropic acid, $C_{10}H_4(OH)_2(SO_3H)_2,NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, brown prisms, m. p. 278° (decomp.), solubility 0·085. p-*Nitrotoluidine* 1 : 8-*diaminonaphthalene*-3 : 6-*disulphonate*,

$$C_{10}H_4(NH_2)_2(SO_3H)_2,(NH_2\cdot C_6H_3Me\cdot NO_2)_2,$$

greyish-tan needles, m. p. 270° (decomp.), solubility 0·186. Mono-α-naphthylamine salt of H-acid, $NH_2\cdot C_{10}H_4(OH)(SO_3H)_2,NH_2\cdot C_{10}H_7$, light violet-grey prisms, m. p. 278° (decomp.), solubility 0·1006. *Mono-ψ-cumidine* salt of H-acid, $C_{10}H_9O_7NS_2,NH_2\cdot C_6H_2Me_3$, grey prisms, m. p. 272° (decomp.), solubility 0·097. Mono-*p*-nitrotoluidine salt of H-acid, $C_{10}H_9O_7NS_2,NH_2\cdot C_6H_3Me\cdot NO_2,H_2O$, grey prisms, m. p. 265° (decomp.), solubility 0·106. Tolidine salt of H-acid, $C_{10}H_9O_7NS_2,NH_2\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2,3H_2O$, greyish-violet prisms, m. p. 260° (decomp.), solubility 0·102. *Zinc* 1 : 8-*diamino*-3 : 6-*disulphonate*, $C_{10}H_4(NH_2)_2S_2O_6Zn,3H_2O$, grey needles,

solubility 6·4; *cobalt* salt, $C_{10}H_4\cdot(NH_2)_2S_2O_6Co,2H_2O$, brown needles solubility 6 at 20°. The solubilities are parts per 100 parts o water, at room temperature unless otherwise specified.

A. J. H.

**Estimation of Anthraquinone.** O. A. NELSON and C. E SENSEMAN (*J. Ind. Eng. Chem.*, 1922, **14**, 956—957).—The following volumetric method has been devised for the estimation o anthraquinone in order to avoid the difficulties of filtration experienced in the method of Lewis (A., 1918, ii, 338). To abou 0·5 gram of the sample of anthraquinone, intimately mixed with 3—4 grams of zinc dust, is added 100 c.c. of boiling 5% sodium hydroxide. After five minutes, the mixture is filtered through asbestos contained in a glass tube, about 24 cm. long and 3·5 cm in diameter, and tapered at one end. This funnel is electrically heated at 90—95° and contains a mechanical stirrer. The red filtrate containing oxanthranol is received in a suction flask and is there directly titrated with a standard solution of potassium permanganate (3·8 grams per litre). Usually three to eight washings of the residue with hot sodium hydroxide solution are necessary in order completely to free it from unreduced anthraquinone, and the apparatus is arranged so that aerial oxidation of the filtrate is prevented. In the titration, the end-point is reached when the filtrate becomes colourless, except when phenanthraquinone is present when a bluish-green colour is obtained which changes to brownish-green on addition of excess of potassium permanganate. Accurate results are obtained hy this method even when the anthraquinone contains phenanthraquinone, anthracene, phenanthrene, phthalic acid, phthalic anhydride, or other oxidation products of anthracene and phenanthrene.

A. J. H.

**A Chemical Method of Assaying the Active Principles of Digitalis.** ARTHUR KNUDSON and MELVIN DRESBACH (*J. Pharm. Expt. Ther.*, 1922, **20**, 205—220).—The pharmacological activity of extracts of digitalis is found to be parallel with the colour developed on treating the digitalis preparation, decolorised with lead acetate, with an alkaline picrate solution. In order to evaluate the activity of the extract, comparison is made in the colorimeter with a standard ouahain solution treated in the same way.

W. O. K.

**The Use of Sodium α-Naphthol-2-sulphonate for the Spectrophotometric Estimation of Aromatic Amino-compounds.** W. E. MATHEWSON (*J. Assoc. Off. Agric. Chem.*, 1922, **6**, 16—28).—The method consists essentially of coupling the naphtholsulphonate with the diazo-compound of the amine, and determining the concentration of the dye photometrically, in comparison with a standard solution of the pure dye. Sodium α-naphtholsulphonate is suited to the purpose because of the ease with which it is to be obtained pure, and to the rapidity and completeness of its reaction with diazo-compounds in dilute solution.

"Extinction coefficients" or "transmissive indices" (Priest, *J. Opt. Soc. Amer.*, 1920, 186) are determined by the König-Martens spectrophotometer, using the light from a mercury vapour lamp. Standard figures for aniline, *o*- and *p*-toluidines, α- and β-naphthylamines, benzidine, anthranilic acid, methyl anthranilate, and *p*-sulphanilic acid are given. The dye from methyl anthranilate is saponified in alkaline solution and direct determinations of its concentration are impossible. In this case the velocity coefficient of saponification is determined; and for purposes of estimation photometric readings are taken at intervals, and the original concentration is determined by calculation. The presence of small quantities of the nitroso-compound of α-naphtholsulphonate has a negligible effect on the transmissive index. Hydrazine may be used in certain cases (for example, β-naphthylamine) to remove excess of nitrous acid, but in others (for instance naphthionic acid) the results obtained are uncertain. Details of the method for estimating amino-impurities in dyes are given. The process may also be used for the estimation of nitrites. A. G. P.

**Pernitric Acid as an Analytical Reagent.** Iv. Trifonov (*Z. anorg. Chem.*, 1922, **124**, 136—139).—Pernitric acid reacts with aniline, yielding an intensely yellow product. The per-acid is formed by the action of hydrogen peroxide on an acidified solution of a nitrite. The above reaction with aniline can therefore be employed for the detection of hydrogen peroxide or a nitrite. Benzene is coloured by pernitric acid yellow, which changes into dark red on the addition of alkali. Toluene and xylene are also coloured yellow but fainter, which, however, does not change on the addition of alkali. Thus benzene in the presence of toluene, xylene, and the aliphatic hydrocarbons can be detected; the aliphatic members are not coloured. Similarly, benzene can be detected in methylated spirits. W. T.

**The Analysis of β-Naphthylamine.** H. R. Lee and D. O. Jones (*J. Ind. Eng. Chem.*, 1922, **14**, 961—963).—Methods for the determination of β-naphthylamine, m. p. 110·1—110·2° (corr.), in the presence of its common impurities, β-naphthol, m. p. 121·2—121·3° (corr.), ββ-dinaphthylamine, m. p. 172·2° (corr.), and α-naphthylamine, m. p. 49·2—49·3° (corr.), are suggested, using specially purified samples of these substances. The direct nitrite titration method usually gives results which are too high, due partly to oxidation of the diazo-β-naphthylamine and partly, when β-naphthol is present, to formation of nitroso-β-naphthol. A more accurate method, based on the fact that β-naphthol-1-sulphonic acid does not absorb nitrous acid, consists of sulphonating 0·65 gram of the sample of β-naphthylamine with 20 c.c. of 25% of fuming sulphuric acid at 0—5° and finally at 15°, diluting the mixture with ice, boiling it to remove sulphur dioxide and afterwards adding 15 c.c. of concentrated hydrochloric acid and estimating the β-naphthylamine by titration with 0·1*N*-sodium nitrite

at 0—5°. For estimation of the β-naphthol present, the sample dissolved in dry benzene is saturated with hydrogen chloride, and after removal of β-naphthylamine hydrochloride by filtration, the β-naphthol in the filtrate is determined by titration with 0·05*N*-*diazotised-p-nitroaniline solution*. *Impurities insoluble in acids* are estimated by boiling 0·5 gram of the sample in 150 c.c. of 1·5% hydrochloric acid, filtering the solution through a Gooch crucible, washing the residue with hot water, and afterwards drying it to constant weight at 100°. Under these conditions, at least 10% of *the β-naphthol passes into the filtrate, but only 0·10—0·20%* of the ββ-dinaphthylamine is soluble, so that this may be extracted from the residue by means of solvents and weighed or analysed for nitrogen. Moisture is determined by drying 5 gram of the finely powdered sample over concentrated sulphuric acid in a vacuum. *A modified Kjeldahl-Gunning method for the estimation* of total nitrogen is described and the melting-point curves of the binary systems, β-naphthylamine–β-naphthol, β-naphthylamine–ββ-dinaphthylamine, and β-naphthylamine–α-naphthylamine are also given. A. J. H.

**Identification of Alanine by Crystallo-chemical Analysis.** Iv. S. Jaitschnikov (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 145—147).—Polarimetric identification of active alanine is sometimes impossible owing to the marked opalescence of the solution. In *such case, use may be made of crystallographic measurements.* The results of the author's measurements are compared with those of Groth and of Fischer (A., 1906, i, 145). T. H. P.

**Detection of Urea. Estimation of Proteolytic Ferments.** Ludwig Pincussen (*Biochem. Z.*, 1922, **132**, 242—244).—Urea is best detected in a liquid free from ammonia by addition of urease at $P_H$ 7·0—7·2, keeping at 55° for fifteen minutes, then addition of two drops of saturated sodium carbonate solution and detection of the production of volatile ammonia by litmus paper. If the liquor contains ammonia originally, it is removed by shaking with powdered permutite, 0·2 gram per c.c.

A quantitative method for estimating proteolytic ferments is described which depends on the micro-Kjeldahl estimation of the non-protein nitrogen formed by the digestion. Unchanged protein is removed by colloidal iron. H. K.

**Detection of the Veronal Group. Diagnosis of Veronal Intoxication.** Heinrich Handorf (*Z. ges. expt. Med.*, 1922, **28**, 56—80; from *Chem. Zentr.*, 1922, iv, 576).—A modification of the murexide test is described for the detection of barbituric acid derivatives in urine. The different members of the veronal group are distinguished by their behaviour when the reaction is carried out in the presence of ammonium chloride, sodium chloride, and barium chloride, respectively. G. W. R.

**Inconstancy of the Precipitation of Uric Acid from Urine in the Form of Cuprous Urate.** J. KHOURI (*Bull. Soc. Chim. Biol.*, 1922, **4**, 375—378).—Denigès's method for the estimation of uric acid in urine gives low and irregular results owing to the incomplete precipitation of the copper salt. This may be remedied to some extent by first treating the urine (100 c.c.) with five drops of sulphuric acid and heating for one hour at 100°. E. S.

**Use of the Newer Indicators in Titrations of Alkaloids.** WILLIAM J. MCGILL (*J. Amer. Chem. Soc.*, 1922, **44**, 2156—2160).—The Sörensen values of aqueous solutions of the hydrochlorides of quinine, cinchonine, morphine, atropine, and strychnine have been determined from *E.M.F.* determinations at various dilutions; measurements were also made in the presence of such quantities of alkali salts as would normally be present in the titration of an alkaloid hydrochloride by alkali. From the results, the most suitable indicators for the titration of such alkaloids are deduced and tested experimentally. It is shown that the indicators generally used in the titration of morphine, atropine, and quinine give results which are not nearly so accurate as should be obtained. Thus in the case of morphine the average error using methyl-red is 1·4%, whereas bromophenol-blue gives an average error of 0·5%, and in some cases it is as low as 0·1%. The most trustworthy indicator for quinine is bromocresol-purple, whilst this indicator is not superior to methyl-red in the titration of cinchona residues. Cochineal and methyl-red give low results with morphine, whilst bromophenol-blue gives a satisfactory value and end-point; the same is also true for atropine and mydriatic residues. Methyl-red can best be used in the titration of strychnine. J. F. S.

**The Estimation of Carnosine in Muscle Extract.** GEORGE HUNTER (*Biochem. J.*, 1922, **16**, 640—654).—Further details are given for the estimation of carnosine in muscle by the application of Koessler and Hanke's diazo-method (this vol., ii, 328). Histidine can be estimated in muscle in the presence of carnosine by utilising Knoop's reaction, since the reaction is not characteristic of carnosine. This fact affords, further, the opportunity of estimating carnosine by a new method, namely, by hydrolysing it and determining the resulting histidine by Knoop's reaction. In ox-muscle, purines are responsible for about 3% of the diazo-colour value reckoned as carnosine, and 2% of the colour may be due to substances other than carnosine. The carnosine content of muscle varies both with the species of the animal and with the individual of the same species. S. S. Z.

**Knoop's Test for Histidine.** GEORGE HUNTER (*Biochem. J.*, 1922, **16**, 637—639).—Different intensities of colour are produced in solutions of the same concentration of histidine by Knoop's test. This is due to the variation in the excess of bromine. The proportion of three atoms of bromine per molecule of histidine is found to give the maximum colour on heating. S. S. Z.

**Precipitation of Proteins by Metaphosphoric Acid. Application to the Analysis of Blood, Pathological Liquids, and Cerebrospinal Fluid.** A. GRIGAUT and P. ZIZINE (*Bull. Soc. Chim. Biol.*, 1922, **4**, 388—406).—In the precipitation of proteins from serum, etc., by means of sodium metaphosphate and hydrochloric acid, the amount of acid employed, provided it is within the limits necessary for the complete precipitation of protein, has little influence on the amount of non-protein nitrogen which passes into the filtrate. Preliminary dilution of the serum, on the other hand, exerts considerable influence; the greater the dilution the smaller the amount of non-protein nitrogen which passes into the filtrate. For serum and pathological liquids the following method is recommended: The serum (10 c.c.) is diluted with water (6 c.c.). A 20% solution of sodium metaphosphate (2 c.c.) is then added, followed by $2N$-hydrochloric acid (2 c.c.). In the case of certain liquids (for instance, whole blood, cerebrospinal fluid) modifications depending on the viscosity and content in protein must be made both in the dilution and the amount of reagents employed. Contrary to the statement of Cristol (this vol., ii, 583), metaphosphoric acid does not produce a partial hydrolysis of the proteins; the higher values obtained with this reagent are probably due to the presence of polypeptides in the filtrate. When trichloroacetic acid is employed these are retained by the proteins in the form of complexes owing to the high acidity of the solution. Metaphosphoric acid has been used for the removal of proteins in the estimation of urea, uric acid, non-protein nitrogen, and dextrose in blood and other fluids. E. S.

**The Gradual Darkening of Hæmatin Solutions in Colorimetric Estimations, and its Prevention.** H. C. GRAM (*Acta med. Scand.*, **56**, 52—70; from *Chem. Zentr.*, 1922, iv, 576).—The darkening of hæmoglobin solutions is not attributed to change of oxyhæmoglobin to hæmatin. It is affected by strength of acid and to a less degree by temperature. It may be prevented, in the Autenrieth method, by addition of 2 c.c. of 3% hydrogen peroxide to 98 c.c. of the hydrochloric acid used. The wedge used for comparison must be specially graduated. The modification is not applicable to the Sahli method. G. W. R.

**Estimation of Pepsin.** MAKI TAKATA (*Tohoku J. Exptl. Med.*, 1921, **2**, 127—130).—One gram of magenta-fibrin is added to gastric juice and the mixture incubated for thirty to forty-five minutes at 38°, then chilled, centrifuged, and the clear liqnid compared colorimetrically with a magenta standard solution.

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**Estimation of Total Protein, of Protein and Non-protein Nitrogen in Blood Plasma.** H. BIERRY and L. MOQUET (*Compt. rend. Soc. biol.*, 1922, **87**, 329—331).—The authors found that in estimating the total proteins in blood by precipitation by heat and weighing the dry precipitate, attention must be directed to the hydrogen-ion concentration of the solution. The amount of precipitate and the quantity of nitrogen contained in it varies, the

maximum being obtained at $p_H = 5{\cdot}6$. Their own procedure is to neutralise 2 c.c. of plasma, diluted to 20 c.c. with water, either with $0{\cdot}01N$-hydrochloric acid or $0{\cdot}1N$-acetic acid, one drop of alizarin being used. This is then boiled for fifteen minutes, and the precipitate collected and dried. The nitrogen is estimated by the regular Kjeldahl method in a portion of the precipitate. The alternative procedure is to measure into a tall cylinder 1 c.c. of plasma, add to it 3 c.c. of acetone free from hydrogen sulphite and leave the precipitate to settle for twelve hours. This is then filtered, washed with acetone, boiling water, boiling alcohol, and finally with ethyl ether. The quantitative results are the same by both methods. CHEMICAL ABSTRACTS.

**Estimation of the Total Non-protein-nitrogen of Serum. Choice of a Suitable Albumin Precipitant.** P. CRISTOL and M. SIMONNET (*J. Pharm. Chim.*, 1922, [vii], **26**, 298—309).—Whilst trichloroacetic acid and tungstic acid are excellent precipitants for albumin in the estimation of the total non-protein-nitrogen of serum, and allow neither lipoid- nor protein-nitrogen to pass into the filtrate, metaphosphoric acid, on the contrary, is unsuitable as complete precipitation is not obtained and the results are always correspondingly high when estimation of total non-protein-nitrogen is in question, although the defecation with this precipitant is sufficiently good for carbohydrate or lactic acid estimations. Of all the precipitants tried, trichloroacetic acid is the best and most convenient, as the estimation of the non-protein-nitrogen can be carried out with as little as 2 c.c. of filtrate, whereas with tungstic acid 5 c.c. of filtrate are required. The evaporation and hydrolysis are more rapid and the estimation more exact. Further, any losses due to too violent ebullition are not to be feared. G. F. M.

**Examination of the Duodenal Fluid obtained through a Tube.** R. DAMADE (*Compt. rend. Soc. biol.*, 1922, **86**, 947—948).—With a 2% solution of methyl-orange the alkalinity of the duodenal fluid was found to vary from 1·4 to 12·5 c.c. of $N$-hydrochloric acid for 10 c.c. Amylase is estimated by determining the amount, in milligrams, of dextrose found in 5 c.c. of 2% starch solution incubated at 37° for one hour with 1 c.c. of the duodenal fluid. This value generally varies from 15 to 35. For the estimation of lipase, 10 c.c. of a 10% solution of ethyl butyrate is treated with 1 c.c. of the duodenal fluid and neutralised to phenolphthalein with $0{\cdot}1N$-sodium carbonate. After incubating the mixture at 37° for one hour, the free acid formed is titrated. Usually 1·2—3·2 c.c. are required. For the estimation of trypsin, 1 c.c. of the fluid is added to 50 c.c. of 5% gelatin solution; this is then neutralised to phenolphthalein and kept at 37° for one hour, 20 c.c. of the digested mixture being titrated with $0{\cdot}1N$-sodium hydroxide solution, whilst another portion of 20 c.c. is titrated after the addition to it of 5 c.c. of formaldehyde solution and 5 c.c. of 90% ethyl alcohol. The tryptic activity is expressed by the sum of the volumes of sodium

hydroxide solution required; the value varies between 4·9 and 7·[illegible] with an average of 5·35 c.c. CHEMICAL ABSTRACTS.

**Detection of Urobilin in Urine.** GEORGES RODILLON (*J. Pharm. Chim.*, 1922, **26**, 379—381).—An alcoholic solution of zin[c] acetate is prepared by mixing 15 grams of zinc oxide with 250 c.c of 95% alcohol and 15 c.c. of glacial acetic acid, and, after fre[-]quently shaking during forty-eight hours, filtering the clear liquid Equal volumes of this reagent and the urine are mixed in a tes[t] tube, 1 drop of a 1 in 10 dilution of tincture of iodine is added an[d] a tenth of the total volume of chloroform. After shaking, th[e] chloroform layer is allowed to separate, and if necessary is clarifie[d] by gentle warming. In presence of urobilin, an emerald-gree[n] fluorescence will be observed when a beam of light is directed o[n] to the chloroform layer. When considerable quantities of urobili[n] are present, the chloroform solution will also show a rose-coloure[d] tint. G. F. M.

**Mechanical Analysis of Humus Soils.** GILBERT WOODIN[G] ROBINSON (*J. Agric. Sci.*, 1922, **12**, 287—291).—The mechanica[l] analysis of peaty soils by the usual methods is frequently of littl[e] value, owing to the cementing together of the finer soil particle[s] by the organic colloids.

The removal of the latter by means of hydrogen peroxide cause[s] a considerable increase in the clay fraction, which by microscopica[l] examination is shown to consist almost entirely of mineral particles.

Ten grams of soil are heated for thirty minutes on a steam-bat[h] with 50 c.c. of hydrogen peroxide (20 vols.). A further treatmen[t] with 25 c.c. of peroxide is usually sufficient to bring about a thoroug[h] dispersion of the soil particles. A. G. P.

**A New Method for the Mechanical Analysis of Soils an[d] Other Suspensions.** GILBERT WOODING ROBINSON (*J. Agric Sci.*, 1922, **12**, 306—321).—The existing method of soil analysi[s] is considerably shortened by the means suggested. A suspensio[n] of soil (2%) in dilute sodium carbonate solution (about 0·025%) i[s] placed in a cylinder and samples are withdrawn by means of a pipette at measured depths and after known periods of settling The results are most conveniently represented by a graphica[l] indication of summation percentages as a function of the logarithm of the settling velocity. By suitable choice of times and depth[s] of sampling, figures corresponding with any of the systems o[f] fractional sedimentation can be obtained. The diameter of th[e] cylinder should not be less than 4 cm. Small errors in the dept[h] of sampling have negligible effects on the final results.

The effect of a gel coating on the settling velocity of a particle i[s] a reduction which is a simple function of the thickness of the gel. It is shown that below the first few centimetres of a settling colum[n] the change in concentration with depth is very small. A. G. P.

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## 1922.

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**2:5-Diketo-1:4-dichloromethylpiperazine** (CHERBULIEZ and FEER), A., i, 1065.

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**2:5-Diketo-1:4-diethoxymethylpiperazine** (CHERBULIEZ and FEER), A., i, 1066.

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**2:5-Diketo-1:4-dimethoxymethyl-2:5-piperazine** (CHERBULIEZ and FEER), A., i, 1065.

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**2:5-Diketo-1:4-dipiperidinomethylpiperazine** (CHERBULIEZ and FEER), A., i, 1065.

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**2:4-Diketo-5-phenyl-5-methyltetrahydro-oxazole** (ALTWEGG and EBIN), A., i, 53.

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**6:7-Dimethoxy-2-phenylquinoline**, and its salts (RILLIET), A., i, 840.
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*ω*-**Dimethylaminopropiophenone,** and its hydrochloride and oxime (MANNICH and HEILNER), A., i, 351.

*α*-**Dimethylaminopyridine** *methiodide* (BROWNING, COHEN, GAUNT, and GULBRANSEN), A., i, 612.

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Invertase.
Lactase.
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**3-Toluene-*p*-sulphonyldextrose** (FREUDENBERG and IVERS), A., i, 524.

**Toluene-*p*-sulphonyldextrosediacetone** (FREUDENBERG and IVERS), A., i, 524.

*o'-p*-***Toluenesulphonyldiphenylnitrosoamine*** (HALBERKANN), A., i, 1132.

**3-*p*-Toluenesulphonyl-2-methylquinoline,** and its salts and derivatives (TRÖGER and MENZEL), A., i, 269.

*p*-**Toluenesulphonyl-2-nitro-3-anilino-*p*-phenetidine** (REVERDIN and ROETHLISBERGER), A., i, 538.

*p*-**Toluenesulphonyl-3:5-*di*nitro-2-anilino-*p*-phenetidine** (REVERDIN and ROETHLISBERGER), A., i, 538.

*p*-**Toluenesulphonyl-2:3-*di*nitro-*N*-methyl-*p*-phenetidine** (REVERDIN and ROETHLISBERGER), A., i, 538.

*p*-**Toluenesulphonyl-*mono*-, *di*- and *tri*-nitro-*p*-phenetidines,** and their derivatives (REVERDIN and ROETHLISBERGER), A., i, 538.

**3-*p*-Toluenesulphonyl-1:3-oxazolid-2-one** (FROMM and HONOLD), A., i, 530.

*p*-**Toluenesulphonyl-*p*-phenetidine,** nitro-derivatives (REVERDIN and ROETHLISBERGER), A., i, 538.

β-*p*-**Toluenesulphonylquinophthalone** (TRÖGER and MENZEL), A., i, 270.

*Toluene compounds, Me* = 1.

**Toluene-*p*-sulphonyltetra-acetylglucose** (FREUDENBERG and IVERS), A., i, 524.

*p*-**Toluenesulphonyl-*p*-tolylsulphoxidethylene** (FROMM and SIEBERT), A., i, 543.

*p*-**Toluenesulphonyl-*p* tolylthiolethane** (FROMM and SIEBERT), A., i, 543.

**Toluene-*p*-sulphonyltriacetylbromoglucose** (FREUDENBERG and IVERS), A., i, 524.

**Toluene-*p*-sulphonyltriacetylmethylglucoside** (FREUDENBERG and IVERS), A., i, 524.

*o*-**Toluic acid,** 3-hydroxy- (ASAHINA and KONDO), A., i, 657.

*p*-**Toluic acid,** bromo-2-amino-, and its derivatives (WHEELER and SMITHEY), A., i, 332.

**Toluic acids,** solubility of, in xylenes (CHAPAS), A., i, 339.

**Toluic acids,** bromo- and chloro-derivatives, and their ethyl esters, amides, bromides, and chlorides (DAVIES *and* PERKIN), *T., 2202.*

*di*nitroamino-, methyl ester, and *tri*-nitro-, and their silver salts and ethyl ester (GIUA), A., i, 534.

**Toluidine** hydrochloride, formation of, from methylaniline hydrochloride (BECKMANN, CORRENS, and LIESCHE), A., i, 535.

hydroferrocyanides (CUMMING), T., 1293.

*o*-**Toluidine,** separation of, from *p*-toluidine (CUMMING), T., 1293.

*m*-**Toluidine,** *di*-ω-chloro- (GOLDSCHMIDT and STROHMENGER), A., i, 1005.

6-iodo-, and its hydrochloride and acetyl derivative (BURTON and KENNER), T., 680.

5-nitro-, preparation of (BRADY, DAY, and ROLT), T., 527.

*p*-**Toluidine,** *2:6-dichloro-*, and *2:6-di*chloro-3-nitro-, and their derivatives (DAVIES), T., 813.

2:3- and 2:5-*di*nitro- (SCOTT and ROBINSON), T., 844.

**Toluidines,** *dinitro-* (BRADY, DAY, and ROLT), T., 526.

**Toluidine-blue,** metachromism of (SCHWARZ and HERRMANN), A., i, 930.

*p*-**Toluidine-*m*-sulphonic acid,** salts of (SCOTT and COHEN), T., 2039.

*o*- and *p*-**Toluidinesulphonitriles,** and their salts (OLIVERI-MANDALÀ), A., i, 1008.

**Toluidinoanthraquinones,** amino- (BADISCHE ANILIN- & SODA-FABRIK), A., i, 942.

*Toluene compounds, Me* = 1.

**4-Toluidinobenzonitriles**, 3-nitro- (MATTAAR), A., i, 251.

*o-p'*-**Toluidinobenzoylbenzene**, *o*-2'-nitro- (MAYER and FREUND), A., i, 866.

*β-p*-**Toluidinobutyric acid**, ethyl ester, and its hydrochloride (STOERMER and ROBERT), A., i, 519.

*p*-**Toluidinoethylitaconic acid**, ethyl ester (CARRIÈRE), A., i, 319.

1-*p*-**Toluidino-2-furyl-5-methylbenziminazole** (FISCHER and MEIER), A., i, 957.

1-*o*-**Toluidino-2-furylnaphthiminazole** (FISCHER and SCHWAPPACHER), A., i, 957.

1-*p*-**Toluidino-2-furylnaphthiminazole**, and its nitrosoamine (FISCHER and MEIER), A., i, 956.

1-*p*-**Toluidino-4-hydroxynaphthalene** (KALLE & Co.), A., i, 824.

1-*p*-**Toluidino-2-*o*-hydroxyphenyl-5-methylbenziminazole**, and its diacetyl derivative (FISCHER and MEIER), A., i, 957.

1-*p*-**Toluidino-2-*o*-hydroxyphenylnaphthiminazole**, and its diacetyl derivative (FISCHER and MEIER), A., i, 956.

1-*o*-**Toluidino-2-hydroxyphenylnaphthiminazoles**, and their derivatives (FISCHER and SCHWAPPACHER), A., i, 957.

3-*p*-**Toluidino-5-keto*iso*oxazole**, and its derivatives (WORRALL), A., i, 874.

3-*p*-**Toluidino-5-ketopyrazole**, and its hydrochloride and acetyl derivative (WORRALL), A., i, 875.

4-*p*-**Toluidino 2-methylanthraquinone**, 1-amino- (BADISCHE ANILIN- & SODA-FABRIK), A., i, 942.

1-*o*-**Toluidino-2-methylnaphthiminazole**, and its acetyl derivative (FISCHER and SCHWAPPACHER), A., i, 957.

6-*o*- and -*p*-**Toluidino-1:4-napthaquinones**,2:3-*di*bromo-5-hydroxy- (WHEELER and ANDREWS), A., i, 354.

1-*o*-**Toluidino-a-naphthiminazole**, and its nitrosoamine (FISCHER and SCHWAPPACHER), A., i, 957.

*β*-**Toluidino-*p*-phenetolecarbamides** (SPECKAN), A., i, 580.

1-*o*-**Toluidino-2-phenyl-a-naphthiminazole**, and its picrate (FISCHER and SCHWAPPACHER), A., i, 957.

1-*p*-**Toluidino-2-phenyl-a-naphthiminazole**, and its nitrosoamine (FISCHER and MEIER), A., i, 957.

2-*p*-**Toluidinophenyl-*p*-tolylsulphone**, and its derivatives (HALBERKANN), A., i, 1133.

*Toluene compounds, Me* = 1.

5-*m*-**Toluidino-1-*m*-tolyl-1:2:3:4-tetrazole** (STOLLÉ), A., i, 689.

*p*-**Toluoylaminobenzoic acids** (LAWRANCE), A., i, 340.

*p*-**Toluoyl-*o*-benzoic acid**, preparation of (MCMULLEN), A., i, 140.

*p*-**Toluoyl-*m*-benzoic acid**, and its silver salt and methyl ester (SMITH), A., i, 141.

**Toluoylbenzoic acids**, aminohydroxy-, hydroxy-, and nitrohydroxy- (EDER and WIDMER), A., i, 261.
*tetra*bromo-, *tetra*iodo- and nitro-, and their methyl esters (LAWRANCE), A., i, 340.

*m*-**Toluoylbenzoic acids**, 3:4- and 3:6-*di*chloro-2-*p*-hydroxy- (V. DEM KNESEBECK and ULLMANN), A., i, 359.

*o*-**Tolyl** *β*-chloroethyl ether, and *p*-nitro- (CLEMO and PERKIN), T., 645.

*p*-**Tolyl** *p'*-amino- and *p'*-nitro-benzy ethers (PUMMERER, MELAMED, anc PUTTFARCKEN), A., i, 1163.
methyl ether, 3-chlorosulphonyl de rivative, preparation of (STEWART) T., 2558.

*p*-**Tolyl-*o*-acetoxystyrylsulphone** (TRÖGER and BOLTE), A., i, 268.

*N*-*o*-**Tolyl-*β*-aminoethyl** hydrogen sul phate (SAUNDERS), T., 2673.

3-**Tolyl-5-anilinomethylene-4-glyoxalones**, 2-thiol- (DAINS, THOMPSON and ASENDORF), A., i, 1185.

*p*-**Tolyl-1-anilino-*m*-tolylsulphone**, an( its derivatives (HALBERKANN), A., i 1134.

*o*- and *p*-**Tolylarsines** (PALMER anc ADAMS), A., i, 786.

1-*p*-**Tolylbenzothiazole**, and its deriv atives (BOGERT and MEYER), A., i 868.

*p*-**Tolyl-*o*-benzoyloxystyrylsulphone** (TRÖGER and BOLTE), A., i, 268.

1-*m*-**Tolyl-4-benzylidenehydantoin**, anc 2-thio- (HILL and KELSEY), A., i 1142.

*p*-**Tolylbiuret** (FROMM and WENZL), A. i, 438.

*a*-*p*-**Tolyl*iso*butyric acid**, *ββ*-*di*chloro (V. AUWERS and ZIEGLER), A., i 140.

*p*-**Tolylcarbamine** cyanide (FROMM anc WENZL), A., i, 438.

**Tolyl-2:4-diacetoxystyrylsulphone** (TRÖGER and BOLTE), A., i, 268.

**Tolyl-2:4-dibenzoyloxystyrylsulphone** (TRÖGER and BOLTE), A., i, 268.

1-*p*-**Tolyl-2:3-dibenzyl-6-methylquinoxaline**, *aa'*-*di*cyano- (DUTT and SEN), T., 2666.

*Toluene compounds, Me* = 1.

*o*- and *p*-**Tolyldi-α-hydroxybenzylarsines** (PALMER and ADAMS), A., i, 786.

*o*- and *p*-**Tolyldi-α-hydroxyethylarsines** (PALMER and ADAMS), A., i, 786.

*m*- and *p*-**Tolyldiphenylmethane**, *di*hydroxy- (MACKENZIE), T., 1698.

**2:4-Tolylenediamine** hydroferrocyanide (CUMMING), T., 1295.
compound of tellurium tetrabromide with (LOWY and DUNBROOK), A., i, 446.

*p*-**Tolylethylcarbinol** (v. AUWERS and KOLLIGS), A., ii, 176.

1-*p*-**Tolyl-4-ethylpyrroline-5-one-3-carboxylic acid**, and its ethyl ester (CARRIÈRE), A., i, 319.

*p*-**Tolylfuryl-2-keto-3-methyl*cyclo*hexylmethane** (WOLFF), A., i, 668.

3-*m*-**Tolyl-4-glyoxalone**, 2-thiol- (DAINS, THOMPSON, and ASENDORF), A., i, 1185.

1-*m*-**Tolylhydantoin**, and 2-thio- (HILL and KELSEY), A., i, 1142.

*p*-**Tolylhydrazine**, *m*-nitro-, preparation of (DAVIES), T., 720.

*p*-**Tolylhydrazinesulphonic acid**, *m*-nitro-, ammonium salt (DAVIES), T., 720.

*p*-**Tolyl-*o*-hydroxystyrylsulphone** (TRÖGER and BOLTE), A., i, 267.

**Tolyl-2:4-*di*hydroxystyrylsulphone**, and its dimethyl ether (TRÖGER and BOLTE), A., i, 268.

*m*-**Tolylideneanthranilic acid** (EKELEY, ROGERS, and SWISHER), A., i, 935.

**5-Tolylimino-2-thio-3-naphthyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole** (GUHA), A., i, 877.

**5-Tolylimino-2-thio-3-phenyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole** (GUHA), A., i, 877.

**5-Tolylimino-2-thio-3-tolyl-2:3:4:5-tetrahydro-1:3:4-thiodiazole** (GUHA), A., i, 876.

*m*-**Tolyl-6-methylbenziminazole** 1:6-hydroxy-, and its salts (JACOBSEN), A., i, 593.

**2-*m*-Tolyl-3-methylindole**, 2-*p*-hydroxy- (v. AUWERS, HILLIGER, and WULF), A., i, 1193.

*o*-**Tolylmethylnitrosoamine** (SCHMIDT and FISCHER), A., i, 822.

**2-*p*-Tolyl-αβ-naphthatriazole**, 6-amino-, and its derivatives and 6-nitro- (MORGAN and CHAZAN), A., i, 181.
9-amino-, and 9-nitro- (MORGAN and GILMOUR), A., i, 380.

*p*-**Tolyl-αβ-naphthatriazoleazo-β-naphthol** (MORGAN and CHAZAN), A., i, 181.

*Toluene compounds, Me* = 1.

α-*o*- and -*p*-**Tolylnaphthylamines**, β-hydroxy- (WAHL and LANTZ), A., i, 823.

**Tolyloxides**, nitro-, lead (GODDARD and WARD), T., 265.

**Tolyloxyacetic acids**, amino-, nitro-, and their derivatives (MINTON and STEPHEN), T., 1594.

2- and 3-*p*′-**Tolyloxy-*p*-cresols**, and their derivatives (PUMMERER, MELAMED, and PUTTFARCKEN), A., i, 1163.

**2-*p*-Tolyloxy-2:3-dihydro-*p*-benzoquinomethane**, and its derivatives (PUMMERER, MELAMED, and PUTTFARCKEN), A., i, 1162.

α-*p*-**Tolylpropionic acid**, ββ*β*-*tri*chloro- (v. AUWERS and JÜLICHER), A., i, 842.

β-*o*-**Tolylpropionolactone**, β-3:5-*di*hydroxy- (LANGLEY and ADAMS), A., i, 1154.

α-*p*-**Tolylprozan-βγ-dicarboxylic acid**, ethyl ester (DIELS and AUBART), A., i, 1194.

1-*p*-**Tolylpyrroline-5-one-3-carboxylic acid**, ethyl ester (CARRIÈRE), A., i, 318.

*o*-**Tolylsulphamic acid**, *p*-amino-, benzoyl derivative, sodium salt (WEIL and WASSERMANN), A., i, 1006.

*p*-**Tolylsulphamic acid**, sodium salt (WEIL and MOSER), A., i, 444.

*o*-**Tolyl-*p*-sulphamsulphonic acid**, amino-, sodium salt (WEIL and WASSERMANN), A., i, 1007.

*p*-**Tolylsulphonyl-*p*-tolylthiolethylene** (*FROMM and SIEBERT*), *A., i, 543.*

1-*p*-**Tolyl-1:2:3:4-tetrazole**, 5-amino- (STOLLÉ), A., i, 689.

*p*-**Tolylthiolacetaldehyde**, phenylhydrazone and tolylmercaptal derivatives of (FROMM and SIEBERT), A., i, 542.

*p*-**Tolylthiolthioacetic acid**, *p*-tolyl ester (FROMM and SIEBERT), A., i, 543.

*m*-**Tolyltoluquinonedi-imide** (GOLDSCHMIDT and STROHMENGER), A., i, 1006.

**Tomato** (*Solanum esculentum*), proteins of the seeds of (JOHNS and GERSDORFF), A., i, 800.

**Toxicity** (RONA and BLOCH; RONA and BACH), A., i, 65; (RONA and REINICKE), A., i, 67; (RONA, AIRILA, and LASNITZKI), A., i, 959.

**Toxins**, formation of, by bacteria (WALBUM), A., i, 902.
chemical nature of (SALKOWSKI), A., i, 1216.
adsorption of, by aluminium hydroxide (RAKUZIN), A., i, 1199.
action of metals on (ERDSTEIN and FÜRTH), A., i, 90.

**Trees,** Indian forest, oils and fats from the seeds of (RAU and SIMONSEN), A., i, 1100.
**Trehalose**, fermentation of, by bacilli (KOSER), A., i, 407.
**Triacetin**, hydrolysis of (YAMAZAKI), A., i, 422.
**3:4:5-Triacetoxystyrene**, ω-nitro- (ROSENMUND and PFANNKUCH), A., i, 1030.
**γεζ-Triacetyl-β-chloroacetylglucose**, α-chloro- (BRIGL), A., i, 225.
**γεζ-Triacetyl-β-*tri*chloroacetylglucose**, α-chloro- (BRIGL), A., i, 225.
**Triacetyl-ethylglucoside-ζ-bromohydrin** (WREDE), A., i, 226.
**Triacetylgallaldehyde**, and its derivatives (ROSENMUND and PFANNKUCH), A., i, 1030.
**γ-εζ-Triacetylglucose**, α- and β-forms of, and its αβ-anhydride (BRIGL), A., i, 1117.
**γεζ-Triacetylglucose**, α-chloro-, and its β-chlorosulphinite and αβ-*di*chloro- (BRIGL), A., i, 225.
**3:5:6-Triacetyl-1-methyl glucosamine** (IRVINE and EARL), T., 2381.
**γεζ-Triacetyl-α-methylglucoside** (BRIGL), A., i, 1117.
**Tri*iso*amylphosphine-ethylimine** (STAUDINGER and HAUSER), A., i, 70.
**Tri*iso*amylphosphinephenylimine** (STAUDINGER and HAUSER), A., i, 70.
**Tri*iso*amylphosphinephenylphosphazide** (STAUDINGER and HAUSER), A., i, 70.
**Trianilinearsine** hydrochloride (SCHMIDT), A., i, 285.
**3:4:5-Tri-*p*-anisyl*iso*oxazole** (MEISENHEIMER and WEIBEZAHN), A., i, 177.
**Triaquotripyridinemagnesium** chloride (SPACU), A., i, 859.
**Triazo-group** (FORSTER and SAVILLE), T., 2595.
**3-Triazocarbazole** (MORGAN and READ), T., 2714.
**α-Triazo-β-hydroxy-β-phenylpropionic acid** (FORSTER and SAVILLE), T., 2595.
**1:2:3-Triazole**, 4:5-*di*cyano-, and its derivatives (GRISCHKEVITSCH-TROCHIMOVSKI), A., i, 724.
**1:2:4-Triazole**, 5-amino-3-thiol-, and 3:5-*di*thiol, and their salts (FROMM KAYSER, BRIEGLEB, and FÖHRENBACH), A., i, 379.
**Triazoles** (ARNDT, MILDE, TSCHENSCHER, BIELICH, and ECKERT), A., i, 277.
synthesis of (FROMM, KAYSER, BRIEGLEB, and FÖHRENBACH), A., i, 377.
**Triazoles**, aromatic, preparation (KALLE & Co.), A., i, 61.
**1:2:3-Triazole-5-carboxylic** aci 4-cyano-, ethyl ester (GRISCHKEVITSCH-TROCHIMOVSKI), A., i, 724.
**α-Triazo-β-methoxy-β-phenylpropionic** acid (FORSTER and SAVILLE), T. 2601.
**Triazosulphole**, and its compound wit mercuric oxide (OLIVERI-MANDALÀ A., i, 1008.
**Tribenzoylgallaldehyde**, and its deri atives (ROSENMUND and PFANNKUCH A., i, 1030.
**Tribenzoylphenylmethane** (MEISENHEIMER and WEIBEZAHN), A., i, 178.
**Tribenzylamine**, *tri-o*-hydroxy-, hydr chloride (ZEMPLÉN and KUNZ), A., 564.
**Tribenzylmethyl chloride** (JONES an SCOTT), A., i, 454.
**Tri*iso*butylcarbinol** (SKRAUP an FREUNDLICH), A., i, 540.
**Tributyrinase**, action of kaolin on th activity of, in serum (OLSEN), A., 292.
**2:4:4-Tricarboxy*cyclo*butane-1-acetic-3-α-propionic acid**, 2-cyano-, ethy ester (INGOLD, PERREN, and THORPE T., 1788.
**2:4:4-Tricarboxy*cyclo*butane-1-malonic-3-α-propionic acid**, 2-cyano-, ethy. ester (INGOLD, PERREN, and THORPE), T., 1788.
*Trichilia emetica*, mafurra tallow from the nuts of (RINDL), A., i, 1102.
*iso***Tricosoic acid**, and its ethyl ester (LEVENE and TAYLOR), A., i, 715.
*iso***Tricosyl** iodide (LEVENE and TAYLOR), A., i, 715.
*iso***Tricosyl alcohol** (LEVENE and TAYLOR), A., i, 715.
*iso***Tricosylmalonic acid**, and its diethyl ester (LEVENE and TAYLOR), A., i, 715.
**Tridymite** from Italy (BILLOWS), A., ii, 578.
**2:4:5-Tri-*p*-ethoxyphenyloxazole** (SCHÖNBERG and KRAEMER), A., i, 664.
**Triethylamine**, action of, on ketopinyl chloride (WEDEKIND and WEINAND), A., i, 549.
**Triethylammonium** ruthenipentabromide (GUTBIER and KRAUSS), A., i, 16.
**Triethylene** *tri-* and *tetra*-sulphides, and their compounds with mercuric salts, and with ethyl iodide (RÂY), T., 1279.
**Triethylphosphinebenzoylimine** (STAUDINGER and HAUSER), A., i, 70.
**Triethylphosphine-ethylimine** (STAUDINGER and HAUSER), A., i, 70.

**Triethylphosphineimineazine** (STAUDINGER and HAUSER), A., i, 70.

**Triethylphosphinemethylimine** (STAUDINGER and HAUSER), A., i, 70.

**Triethylphosphinephenylimine** (STAUDINGER and HAUSER), A., i, 70.

**Triethylsulphonium** bromide, absorption spectra of, in various solvents (TAYLOR and LEWIS), T., 665.

**β-Trigalloyllævoglucosan,** and its potassium salt (KARRER and SALOMON), A., i, 267.

**Triglycolamidic acid,** tri-*p*-anisylamide of (HILL and KELSEY), A., i, 1141.

**Trihexosan,** and its nona-acetyl derivative (PICTET and JAHN), A., i, 987.

**2:3:5-Triketo-6-α-methoxybenzyl-1:4-dimethylpiperazine** (FORSTER and SAVILLE), T., 824.

**2:3:5-Triketo-6-α-methoxybenzyl-1(or 4)-methylpiperazine** (FORSTER and SAVILLE), T., 824.

**2:4:5-Trimercuriacetanilide,** acetate of (ROSSI), A., i, 605.

**2:3:5-Trimethoxybenzoic acid** (FALTIS and NEUMANN), A., i, 570.

**2:4:4′-Trimethoxybenzophenone** (ZIEGLER and OCHS), A., i, 1049.

**2:4:5-Trimethoxybenzylideneanthranilic acid** (EKELEY, ROGERS, and SWISHER), A., i, 935.

**6:7:8-Trimethoxy-1:2-dimethyl-1:2:3:4-tetrahydro*iso*quinoline,** salts of (SPÄTH), A., i, 165.

**7:5′:6′-Trimethoxy-2-ethyl-3:4-indeno-(2′:1′)-benzopyrylium** ferrichloride (CRABTREE and ROBINSON), T., 1037.

**Trimethoxy-β gambier-catechincarboxylic acid** (NIERENSTEIN), T., 28.

**6:7:8-Trimethoxy-1-methyl-3:4-dihydro*iso*quinoline,** and its salts (SPÄTH), A., i, 165.

**7:5′:6′-Trimethoxy-2-methyl-3:4-indeno-(2′:1)-benzopyrylium** ferrichloride (CRABTREE and ROBINSON), T., 1036.

**6:7:8-Trimethoxy-1-methyl-1:2:3:4-tetrahydro*iso*quinoline,** salts of (SPÄTH), A., i, 165.

**2:3:4-Trimethoxyphenyl styryl ketone** (BRAND and COLLISCHONN), A., i, 452.

**6:7:8-Trimethoxy-1:2:3:4-tetrahydro*iso*quinoline, and its salts** (SPÄTH), A., i, 165.

**Trimethylamine** chlorite (LEVI), A., i, 528.
hydroferrocyanide (CUMMING), T., 1297.

**Trimethylammonium** ruthenipentabromide (GUTBIER and KRAUSS), A., i, 16.

**2:3:5-Trimethylaniline,** 4(?)-chloro- (GOLDSCHMIDT and STROHMENGER), A., i, 1005.

**2:3:4-Trimethylbenzaldehyde,** 6-hydroxy-, and its semicarbazone (v. AUWERS and ZIEGLER), A., i, 121.

**2:3:5-Trimethylbenzene,** 1-*di*chloroamino- (GOLDSCHMIDT and STROHMENGER), A., i, 1005.

**ββγ-Trimethylbutane** (CHAVANNE and LEJEUNE), A., i, 417.

**βγγ-Trimethyl-Δα-butylene** (CHAVANNE and LEJEUNE), A., i, 417.

**ααβ-Trimethylbutyric acid,** β-hydroxy-, ethyl ester (LEROIDE), A., i, 218.

**Trimethylcamphorylmethylammonium** bromide, preparation of (RUPE), A., i, 666.

**1:2:3-Trimethyl-5-*di*-ω-chloroethylbenzene** (v. AUWERS and ZIEGLER), A., i, 121.

**1:2:6-Trimethyl-1-*di*chloromethyl-Δ2:5-*cyclo*hexadien-4-one,** and its derivatives (v. AUWERS and ZIEGLER), A., i, 121.

**1:3:6-Trimethyl-1-*di*chloromethyl-Δ2:5-*cyclo*hexadien-4-one,** 5-chloro- (v. AUWERS and ZIEGLER), A., i, 145.

**1:7:9-Trimethyldeoxyuric acid,** and its salts (BILTZ and BÜLOW), A., i, 383.

**3:4:5-Trimethyl-2:6-dibromomethylphenol** (v. AUWERS and SAURWEIN), A., i, 1033.

**3:4:5-Trimethyl-2:6-dihydroxymethylphenol** (v. AUWERS and SAURWEIN), A., i, 1033.

**Trimethylene** chlorobromide, action of, on aliphatic ketones (BILLON), A., i, 717.
dinitrate (BLECHTA), A., i, 518.

**2:4:5-Tri-*mp*-methylenedioxyphenyloxazole** (SCHÖNBERG and KRAEMER), A., i, 665.

**Trimethylene glycol,** poly-ethers of (ROJAHN), A., i, 103.
preparation of, β-bromo- and β-chloropropionic acids from (ROJAHN), A., i, 105.
estimation of, in crude glycerol (COCKS and SALWAY), A., ii, 232.

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# ERRATA.

## Vol. 104 (Abstr., 1913).

| Page | Line | |
|---|---|---|
| i. 681 | 11 | *for* "4-$\beta$-iminoethylglyoxaline" *read* "4-$\beta$-aminoethylglyoxaline." |

## Vol. 106 (Abstr., 1914).

| | | |
|---|---|---|
| ii. 135 | 10* | *for* "**Thorium**" *read* "**Thallium.**" |
| ii. 874 | 8* | col. ii. *for* "thorium" *read* "thallium." |

## Vol. 108 (Abstr., 1915).

| | | |
|---|---|---|
| i. 719 | 8* | delete "Vernier." |
| ii. 891 | 17 col. ii. | ,, "**Vernier.**" |
| ii. 965 | 29 col. ii. | ,, "**Vernier** *see Léon* **Givaudin.**" |
| ii. 1103 | 18 col. i., 26 | ,, "Vernier." |

## Vol. 120 (Abstr., 1921).

| | | |
|---|---|---|
| i. 165 | 25 | *for* "Zeigler" *read* "Ziegler." |
| i. 796 | 16* | ,, "ethyl *r*-pinate" *read* "ethyl *r*-pinonate." |

## Vol. 122 (Abstr., 1922).

| | | |
|---|---|---|
| i. 224 | 24 | for "*Digitoxone*" read "*Digitoxose.*" |
| i. 319 | 1* | ,, "*furfuran*" read "*furan.*" |
| i. 371 | 18 | ,, "*Bis*-1:3′-*indyl*" read "*Bis*-1:3′-*indil.*" |
| | 22 | ,, "3:3′-*indyl*" read "3:3′-*indil.*" |
| | 27 | ,, "1:1′-*indyl*" read "1:1′-*indil.*" |
| | 31 | ,, "3:3′-*Methylketyl* (3:3′-*dimethylketoyl*)" read "2:2′-*Dimethyl* 3:3′-*indil* (2:2′-*dimethyl*-3:3′-*diindoyl*)." |
| i. 554 | 17 | ,, "Schlichtung" *read* "Schlichting." |
| i. 563 | 16 | ,, "Telecky" *read* "Teleczky." |
| i. 758 | 25 | ,, "*bis-3-carbethoxy-2:4-dimethylpyrrylmethene*" read "*ethyl methenylbis-2:4-dimethylpyrrole-3-carboxylate.*" |
| i. 758 | 17* | ,, "$CO_2Et·C:Me$ / $MeC=N$ >C= etc." *read* "$CO_2Et·C:CMe$ / $MeC{=}{=}N$ >C= etc." |
| i. 848 | 13* | *insert* "[cf. Stevens, A., 1921, i, 735]." |
| i. 945 | 13 | for "*Cympopogan*" read "*Cymbopogon.*" |
| ii. 77 | 8 | ,, "$PbO,5UO_3,4H_2O$" *read* "$2PbO,5UO_3,4H_2O$." |
| ii. 415 | 20 | ,, "**122**" *read* "**121.**" |
| ii. 519 | 18* | ,, "Kanaker" *read* "Karraker." |
| ii. 582 | bottom | ,, "30% of hydrogen peroxide" *read* "30% hydrogen peroxide." |
| ii. 685 | 3 | ,, "christobalite" *read* "cristobalite." |
| ii. 710 | 16* | ,, "lead tetraethyl" *read* "magnesium ethyl iodide." |
| ii. 714 | 5 | ,, "*naurite*" read "*nauruite.*" |
| ii. 714 | 12 | ,, "variszite" *read* "variscite." |
| ii. 768 | 2* | ,, "Halle" *read* "Halla." |
| ii. 830 | 13* | ,, "Hammersten" *read* "Hammarsten." |

* From bottom.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 19th, 1922, at 8 p.m., SIR JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

| | Elected. | Died. |
|---|---|---|
| Giacomo Ciamician (Honorary Fellow) ... | March 2nd, 1911 | |
| Ganesh Sakharan Agashe ................. | June 15th, 1916 | Dec. 2nd, 1921 |
| James Albert Allison .......................... | Dec. 7th, 1905 | Dec. 9th, 1921 |
| Charles Edward Cassal ........................ | Feb. 6th, 1899 | Dec. 22nd, 1921 |
| William King .................................... | June 21st, 1917 | Nov. 7th, 1921 |

The PRESIDENT announced:

(1) That in accordance with the Bye-laws the following vacant places fall due to be filled at the Annual General Meeting on March 30th, 1922:

| | |
|---|---|
| Vice-Presidents who have filled the office of President .. .. .. .. .. | Two vacancies. |
| Vice-Presidents who have not filled the office of President .. .. .. .. .. | Two vacancies. |
| Secretary .. .. .. .. .. .. | One vacancy. |
| Ordinary Members of Council: | |
| (*a*) Town Members (that is, those living within a radius of 50 miles from London) | Three vacancies. |
| (*b*) Country Members (that is, those living beyond a radius of 50 miles of London) | Three vacancies. |

The Council has nominated Dr. Irvine Masson to the office of Secretary.

The names of the Members of Council who retire at the Annual General Meeting on March 30th, 1922, and who are ineligible for re-election to the same office until the lapse of one year, are as follows:

Vice-Presidents who have filled the office of President:

Sir James J. Dobbie and Sir William J. Pope.

Vice-Presidents who have not filled the office of President:

Professor J. B. Cohen and Dr. H. J. H. Fenton.

Ordinary Members of Council:

(*a*) Town Members:

Mr. J. A. Gardner, Dr. C. A. Keane, and Sir Robert Robertson.

(*b*) Country Members:

Dr. E. F. Armstrong, Professor F. E. Francis, and Principal J. C. Irvine.

(2) That arrangements have been made with the Society of Chemical Industry whereby provincial Local Sections of that Society may give opportunity to Fellows of the Chemical Society to read papers on pure chemistry and to attend the meetings at which such papers are read. Further information in regard to the scheme will be circulated at an early date.

(3) That a pamphlet entitled "Notes on the Furnishing and Equipment of Chemical Laboratories" has just been issued by the Society. Arising from a Conference held in July, 1920, to consider whether economies could be effected in the equipment of chemical laboratories, a small Committee was appointed by the Council to look into and report upon the matter. These "Notes" represent the results of the inquiry and can be obtained free of charge on application to the Assistant Secretary.

Certificates were read for the first time in favour of:

Jnanendra Kumar Adhya, M.Sc., 30, Judge's Court Road, Alipore, Calcutta.
Gilbert James Avey, Northern Polytechnic Institute, Holloway, N. 7.
Bhagwan Das Batta, B.Sc., F. C. College, Lahore, India.
Darrell Webb Beesley, A.I.C., 29, King Edward Road, Dentons Green, St. Helens.
William Alfred Bishop, B.A., 33, Banstead Road, Purley.
Leslie James Burrage, B.Sc., 32, Emerson Road, Ilford.
Gabriel Cofman-Nicoresti, 15, Ludlow Road, Ealing, W. 5.
Archibald Neil Currie, M.A., B.Sc., A.I.C., 44, Fisher Street, Dennistoun, Glasgow.
James Owen Chesshyre Dalton, B.A., The Plot, Adams Road, Cambridge.
Arthur William Edwards, 4, Dunvegan Road, Eltham, S.E. 9.
Samuel Ellingworth, M.Sc., 74, Millfield Road, York.
Kenneth Fisher, M.A., Ph.D., Eton College, Windsor.
Miri Lal Goel, M.Sc., Royal Artillery Bazar, Ambala, India.
George Grimshaw Hammond, B.Sc., 254, Mill Street, Toxteth, Liverpool.
William Allen Hamor, M.A., Mellon Institute of Industrial Research, The University, Pittsburg, Pa., U.S.A.
Frank Mouat Irvine, B.Sc., A.I.C., 30, Clayton Road, Jesmond, Newcastle-on-Tyne.

John Albert Jenkinson, B.Sc., School House, Little Sutton, Birkenhead.
Rowland Nicholas Johnson, B.Sc., Greenstede, West Hill, East Grinstead.
David John Lake, B.Sc., 36, Gerald Street, Hafod, Swansea.
Herbert Langwell, Wentworth, Denham Road, Epsom.
Vernon Howes Legg, B.Sc., 95, Carter Knowle Road, Sheffield.
John Alexander McRae, M.A., Ph.D., F.I.C., Queen's University, Kingston, Ont., Canada.
Walter Thomas James Morgan, 171, Kensington Avenue, Manor Park, E. 12.
John Sydney Morrison, 23, Seymour Road, Cheadle Hulme, Manchester.
Partridge Leslie Podd, B.Sc., 8, St. Peter's Street, Ipswich.
Krishnarajpet Venkata Rau, B.A., B.Sc., Ananda College, Colombo, Ceylon.
Frank Crafer Ray, B.A., 47, Alfriston Road, Clapham Common, S.W. 11.
Jessie Stewart, B.Sc., School House, Helmington Row, Crook, Co. Durham.
George Taylor, Frigorifico, Campana F.C.C.A., Argentine.
James Rawson Walmsley, A.I.C., Dean Brook Cottage, Dean Lane, Moston, Manchester.
Walter Arthur White, 144, Shelley Avenue, Manor Park, E. 12.
Robert Norman Wright, B.Sc., A.I.C., 16, Redcliffe Street, S. Kensington, S.W. 10.

Prof. A. SMITHELLS then gave an account of the Lewis-Langmuir theory of atomic structure, the exposition being illustrated with a large number of models. On the motion of Prof. Sir W. H. Bragg, supported by Prof. Lowry and the President, a cordial vote of thanks to the lecturer was passed with acclamation, and Prof. Smithells made suitable acknowledgment.

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## ORDINARY SCIENTIFIC MEETING.

The next Ordinary Scientific Meeting will be held on Thursday, February 2nd, 1922, at 8 p.m.

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## LECTURE.

At the Ordinary Scientific Meeting to be held on Thursday, February 9th, 1922, at 8 p.m., in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, S.W.1., Sir Ernest Rutherford, M.A., D.Sc., F.R.S., will deliver his Lecture, entitled " Artificial Disintegration of Elements."

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## SETS OF THE BERICHTE AND OF THE ZENTRALBLATT.

The Council has secured a few sets of the *Berichte* and of the *Zentralblatt* from August, 1914, to December, 1920, inclusive. These can be obtained, *in complete sets only*, from the Assistant Secretary, price £10 a set of the *Berichte*, or of the *Zentralblatt*.

The number of sets is strictly limited, and applications will be dealt with in the order in which they are received.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

DEUTSCHE CHEMISCHE GESELLSCHAFT. Chemisches Zentralblatt. Generalregister IV, über die Jahrgänge 1912–1916. Edited by IGNAZ BLOCH. Leipzig 1921. pp. vi + 2016. (*Reference.*)

From the Deutsche Chemische Gesellschaft.

FÉDÉRATION DES INDUSTRIES CHIMIQUES DE BELGIQUE. Bulletin. Vol. I., etc. Gand 1921 +. [Issued with the *Bull Soc. Chim. Belg.*] (*Reference.*)

From the Société Chimique de Belgique.

FOURNEAU, ERNEST. Préparation des médicaments organiques. Paris 1921. pp. viii + 350. 25 *fr.* (*Recd.* 13/12/21.)

From the Author.

PARKES, SAMUEL. The rudiments of chemistry; illustrated by experiments, and eight copper-plate engravings of chemical apparatus. London 1810. pp. xii + 294. ill. (*Reference.*)

From Mr. W. Livingstone Gunn.

### II. *By Purchase.*

FISCHER, FERDINAND. Kraftgas: Theorie und Praxis der Vergasung fester Brennstoffe. (*Chem. Tech. in Einzeldarstellungen.*) 2nd edition. Edited by J. GWOSDZ. Leipzig 1921. pp. iii + 428. ill. (*Recd.* 21/12/21.)

MINISTRY OF MUNITIONS and DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. Technical records of explosives supply. 1915–1918. No. IV. The theory and practice of acid mixing. London 1921. pp. vi + 94. ill. 12*s.* net. (*Recd.* 8/12/21.)

VANINO, LUDWIG. Handbuch der präparativen Chemie. 2nd edition. Vol. I. Anorganischer Teil. Stuttgart 1921. pp. xxiv + 21. ill. (*Recd.* 13/12/21.)

### III. *Pamphlets.*

MEES, CHARLES EDWARD KENNETH, and CLARKE, HANS THATCHER. The preparation of synthetic organic chemicals at Rochester. [A lecture delivered before the Society of Chemical Industry, Montreal, August 31, 1921.] Rochester, N.Y. 1921. pp. 40. ill.

MOIR, JAMES. (1) The permanganate absorption-spectrum: a claim for priority. (2) A formula for calculating the uranium spectrum. (From the *Trans. Roy. Soc. S. Africa*, 1921. **10.**)

Scientific and Industrial Research, Department of. Bulletin No. 5. The cleaning and restoration of museum exhibits: report upon investigations conducted at the British Museum. London 1921. pp. 12. ill.

—— First report of the Gas Cylinders Research Committee. London 1921. pp. 126. ill.

—— *Food Investigation Board.* Special Report No. 5. Report on heat insulators by the Engineering Committee of the Food Investigation Board. Experiments by Ezer Griffiths. London 1921. pp. 61. ill.

—— *Fuel Research Board.* Technical Paper No. 3. The efficiency of low temperature coke in domestic appliances. By Margaret White Fishenden. London 1921. pp. 35. ill.

Wright, Allister MacLean. The anticomplementary properties observed in certain serum reactions. (From the *Trans. New Zealand Inst.*, 1921, **53**.)

Wright, *Allister MacLean, Bevis, Miss J. F., and the late* Percy S. Nelson. The chemistry of flesh foods. No. 5. The nitrogenous constituents of meat-extracts. (From the *Trans. New Zealand Inst.*, 1921, **53**.)

## CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, FEBRUARY 16TH, 1922.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Adhya, Jnanendra Kumar, M.Sc. (Cal.), 30, Judge's Court Road, Alipore, Calcutta. Chemical Laboratory Assistant, Govt. Test House, Alipore, Calcutta. Took the M.Sc. degree of the Calcutta University in 1920. Served as an asst. chemist in the Research Dept. of Messrs. Bird & Co., Calcutta. At present employed as a Chemical Laboratory Assistant, Govt. Test House, Alipore, Calcutta. Late Hon. Secretary, Presidency College Chemical Society, Calcutta. (*Signed by*) N. Brodie, J. Bhaduri, B. B. Dey.

Applebee, Harry Charles, 509, Edge Lane, Droylsden, nr. Manchester. Chief Works Chemist, Manchester Corporation Gas Works, Bradford Road, Manc. Finsbury Technical College (Chemical Department), 1902–1905 (*Certificate*). *Associate of the Institute* of Chemistry (1918). Lecturer, Chemistry of Gas Manufacture, Manchester College of Technology. (*Signed by*) E. F. Morris, F. M. Rowe, Frank Lee Pyman, F. S. Sinnatt, E. Williams.

Avey, Gilbert James, Chemical Department, Northern Polytechnic *Institute, Holloway, London*, N. 7. Lecturer in Chemistry. Wish to receive the Journals of the Society. (*Signed by*) T. J. Drakeley, Raymond R. Butler, Philip Schidrowitz.

Baker, John William, 20, Redfield Lane, Earls Court Rd., S.W.5. Research Student in Organic Chemistry at the Imperial Coll. of Science and Technology. Royal Scholarship in Chemistry, 1916. A.R.C.S. Chem., First Class, 1921. B.Sc. Hons. Chem., First Class, 1921 (London). (*Signed by*) Jocelyn Thorpe, James C. Philip, M. A. Whiteley, C. K. Ingold.

Batta, Bhagwan Das, Nabha State, Panjab (India). Demonstrator in Chemistry, F. C. College, Lahore. Appearing for the Panjab University M.Sc. Degree. B.Sc., Panjab University. Demonstrator in chemistry at Forman Christian College, Lahore. Working on the "Active principle of *Meliā Aziderācta* (India) leaves." (*Signed by*) N. A. Yajnik, Edwin Theodore Dean, S. R. Khosla.

Beesley, Darrell Webb, 29, King Edward Rd., Dentons Green, St. Helens. Technical Chemist. Associate of Institute of Chemistry. Asst. works manager, Messrs. Tennants (Lancs.), Ltd., Manchester; previously head chemist for same; prior to this, asst. chemist with United Alkali Co. (*Signed by*) Chas. W. Carpenter, E. L. Rhead, Wm. E. Kay.

Bishop, William Alfred, 33, Banstead Rd., Purley, Surrey. Chemist. B.A. Cantab. (*Signed by*) H. J. H. Fenton, C. T. Heycock, F. W. Dootson.

Brisley, Charles William, 105, Thurlow Park Road, London, S.E.21. Student at University of Oxford. B.A. Honours (Chemistry). At present doing research for Part II. School of Natural Science (Chemistry). (*Signed by*) F. D. Chattaway, E. Hope, S. G. P. Plant, M. P. Applebey, L. Gowing-Scopes.

Burke, Katharine Alice, 17, Lion Gate Gardens, Richmond, Surrey. Assistant Lecturer in Chemistry, University College, W.C.1. B.Sc. London. Published papers in the *Journal of the Chemical Society*, and *Zeitschrift für Physikalische Chemie*. Translated "Thermochemistry," by Julius Thomsen, in Sir Wm. Ramsay's series. (*Signed by*) J. N. Collie, Irvine Masson, F. G. Donnan.

Burrage, Leslie James, 32, Emerson Road, Ilford, Essex. Undergraduate at King's College, London. Taking Hons. B.Sc., Chemistry (Oct. 1921). B.Sc. degree obtained Oct. 1921. Being now engaged on research work at King's College I wish to keep in touch with fresh chemical developments. (*Signed by*) Arthur Fairbourne, A. J. Allmand, Harold Toms.

Byles, John Edward, 87, Newlands Park, Sydenham, S.E.26. Chemist, Class II, Government Laboratory. B.Sc. (Manchester), A.I.C. Nine years at Government Laboratory. (*Signed by*) A. G. Francis, F. S. Aumonier, J. R. Nicholls.

Child, Reginald, Yateley Lodge Cottage, Yateley, Camberley. Honours Student of King's College, London. (*Signed by*) Samuel Smiles, H. W. Cremer, C. S. Salmon.

Christie, George Hallatt, 155, Sharrow Vale Rd., Sheffield. Engaged in Research in Organic Chemistry with Dr. J. Kenner, Sheffield University. Master of Science (1st Class Hons. Chemistry, Sheffield University). Organic Chemical Research under Dr. Kenner since June 1920. I wish to have access to the Society's Library and receive the Society's Journal. (*Signed by*) W. P. Wynne, J. Kenner, F. G. Tryhorn, A. W. Chapman, Thos. B. Smith.

Cofman-Nicoresti, Gabriel, 15, Ludlow Road, Ealing, W.5. Pharmacist Manufacturing Chemist, Member of the Pharmaceutical Society. Director of the Solidol Chemical Co., Mill Street, Dockhead, S.E.1. Inventor and patentee of improvements in or connected with stoves for burning solidified spirit or the like, No. 101569/16, and also improved liniment, No. 18060/15. I desire to make use of the Library and keep in touch with current chemical

literature. (*Signed by*) Jules Cofman-Nicoresti, Hartley Shaw, S. B. Tallantyre.

COURTNEY, WILLIAM BARRY, 12, Caithness Road, Mitcham, Surrey. Student, engaged on research work. I have been a student of the Chemical Department of the South-Western Polytechnic Institute for five years, and have passed the B.Sc. (Honours) examination of the London University in Oct. 1921. (*Signed by*) J. B. Coleman, F. H. Lowe, F. Arnall, J. C. Crocker.

CRUTCHLON, BERNARD WILLIAM ALFRED, 65, Durlston Rd., Upper Clapton, E.5. Honours Student of King's College, London. (*Signed by*) Samuel Smiles, H. W. Cremer, C. S. Salmon.

CURRIE, ARCHIBALD NEIL, M.A., B.Sc. A.I.C., 44, Fisher St., Dennistoun, Glasgow. (The applicant holds the Glasgow University B.Sc. degree with special distinction in his principal subject—Chemistry.) Biochemist to the Glasgow Royal Cancer Hospital. The applicant has two papers ready for publication. The first is "The Fat of Adipose Tissue in Malignant Disease," and will be published shortly either as a Hospital Bulletin or in the *Journal of Exptl. Pathology and Bacteriology*. The second, which is one of a series of "Studies in Fat Pigment," is entitled: "A Preliminary Note on the Separation of Pigment from Accompanying Fat." (*Signed by*) G. G. Henderson, T. S. Patterson, J. Roberts.

DALTON, JAMES OWEN CHESSHYRE, The Plot, Adams Road, Cambridge. Engaged in Research work at Cambridge University. Honours Degree in Nat. Science Tripos Part II., June 1921. (*Signed by*) W. J. Pope, T. M. Lowry, W. H. Mills.

EDWARDS, ARTHUR WILLIAM, 4, Dunvegan Road, Eltham, S.E.9. Chemist. (1) Early education at Dorchester Grammar School; winner of the science prize in 1902. (2) Studied Analytical Chemistry and Physics at Duncan's School of Pharmacy under Mr. William Duncan, F.C.S., Ph.C., also at Darlington Technical College, and under private tutors. (3) Matriculated at Edinburgh University in 1909, for the study of chemistry. (4) Passed the minor examination of the Pharmaceutical Society of Great Britain in 1909; Member of the British Pharmaceutical Conference. (5) Engaged in bacteriological and pharmaceutical chemistry under Mr. J. E. Langford Moore, F.C.S., at St. Bartholomew's Hospital. (6) For five years with the English Company of Farbenfabriken vorm. Friedrich Bayer & Co., Elberfeld and Leverkusen, under Dr. C. R. Henning, Ph.D., F.C.S. (7) Served in the Royal Engineers—gas services—during the War. (8) At present with Messrs. R. W. Greeff & Co., Ltd., of Thames House, Queen Street Place, E.C.4, in an advisory and technical capacity. (9) Keenly desirous of keeping in touch with up-to-date Chemical Research and receiving the publications of the Chemical Society. (*Signed by*) J. E. Langford Moore, Percy Barrs, Frank B. Arnold, William Duncan, Charles Cockle.

ELLINGWORTH, SAMUEL, 74, Millfield Road, York. Research Chemist, Dept. of Organic Chemistry, University of Leeds. B.Sc. (Leeds), 1st Class Honours, 1916. M.Sc. 1918. Chemist to the British Dyestuffs Corporation (Huddersfield), Ltd. (1916–1921). (*Signed by*) J. B. Cohen, P. K. Dutt, Arthur Smithells, Akira Shimomura.

FISHER, KENNETH, Eton College. Schoolmaster. M.A. (Oxon), Ph.D. (Jena). (*Signed by*) W. H. Perkin, D. Ll. Hammick, R. H. Thomas, T. W. J. Taylor, E. Hope, N. V. Sidgwick.

FREDERIKSE, WILLIAM ALEXANDER, Amsterdam, Honthorststraat 2. Chemical Student, University of Amsterdam. Qualifications none. Desires to become a fellow of the Chemical Society, in order to profit by the Journal

and other publications. (*Signed by*) H J. Backer, J. C. Irvine, R. Robinson.

GOEL, MIRI LAL, Royal Artillery Bazar, Ambala, Punjab (India). 2nd Professor of Chemistry, Meerut College, Meerut (U.P.). B.Sc. with Honours in Chemistry; M.Sc. of the Punjab University; Research Scholar of the Punjab University for some time; Demonstrator of the B.Sc. IV year class Govt. College Chem. Lab. while student of the M.Sc. class; Professor of the Divisional College, Meerut (U.P.), since November 1919, taking both Intermediate and B.Sc. classes. Joint author of the paper published in J.C.S. (Trans., 210; 1921 Feb.); worked as Consulting Chemist of the Goel Scientific and Technical Works, Meerut; Organised "Iswar" Soap Factory, R.A. Bazar, Ambala; doing research work on essential oils and dyeing extracts from vegetable dyestuffs in the College at present. (*Signed by*) Horace B. Dunnicliff, N. A. Yajnik, Edwin Theodore Dean, Shanti Swarupa Bhatnagar, Bawa Kartar Singh.

GOSS, FRANK ROBERT, 4, Abbotsford Rd., Goodmayes, Ilford, Essex. Neil Arnott Research Scholar of the University of London. Student from 1918 to 1921 at the Royal College of Science, obtaining on completion of course the Associateship (A.R.C.S.) in Chemistry, and B.Sc. (Lond.) with Honours in Chemistry. I have been awarded the Neil Arnott Medal in Chemistry of the Univ. of London, and am at present working in the Organic Chemistry Research Laboratories of the Royal Coll. of Science. (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, C. K. Ingold.

GREY, EGERTON CHARLES, Medical School, Cairo, Egypt. Professor of Chemistry. D.Sc., M.B. Author of several papers on the Chemical Action of Bacteria, published in the Proc. of the Royal Society. (*Signed by*) Arthur Harden, F. R. Henley, Robert Robison, Ida Smedley Maclean.

GRIMWOOD, ROBERT CHARLES, 11, Billiter Square, E.C.3. Research Student, Royal College of Science. Associate City and Guilds, Finsbury Institute. Registered Student at Institute of Chemistry. (*Signed by*) Jocelyn Thorpe, Robt. G. Grimwood, M. A. Whiteley, C. K. Ingold.

HAMMOND, GEORGE GRIMSHAW, 254, Mill Street, Toxteth, Liverpool. Analyst and Chemist. Bachelor of Science (Manchester). Member of The Pharmaceutical Society. (*Signed by*) Arthur W. Duncan, Frederick Owen, Walter Salmon.

HAMOR, WILLIAM ALLEN, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., U.S.A. Assistant Director of the Mellon Institute of Industrial Research. Educated, University of Pittsburgh, 1904–1907; Master of Arts, 1913. Research Chemist, College of the City of New York, 1907–1914. Assistant to the Director, Mellon Institute, Pittsburgh, Pa., 1914–1916. Assistant Director, Mellon Institute, since 1916. Shale Oil Expert, Department of Mines of Canada, 1908. Editorial Staff, *Journal of Industrial and Engineering Chemistry*, 1912-1914. Editorial Board Member, "The Science History of the Universe," 1909. Commissioned a Major in the Chemical Warfare Service, United States Army, November 28, 1917; served in France ten months as assistant chief of the Technical Division, C.W.S., A.E.F.; honourably discharged, December 6, 1918. Member of the National Research Council on the Division of Research Extension, 1921–1924. Member of the National Research Council's Sub-Committee on Airplane Fuels, 1917. Member of various committees of the American Chemical Society, 1913–1921. Specialist in hydrocarbon chemistry. Author of the following books: "A History of Chemistry," 1909; "The American Petroleum Industry" (with R. F. Bacon), 2 vols., 1916; "The Examination

of Petroleum" (with F. W. Padgett), 1920; and "American Fuels" (with R. F. Bacon), 2 vols., 1922. Also author of a series of papers and reports of researches on oil-shales, petroleum, fuels, and anæsthetics. Contributor to scientific journals on educational subjects, especially on the value of industrial research and chemistry. Member of the *American Chemical* Society, American Electrochemical Society, and Alpha Chi Sigma and Phi Lambda Upsilon fraternities. Residence: 1030, *Victoria Avenue*, New Kensington, Pa. Business Address, Mellon Institute of Industrial Research, Pittsburgh, Pa., U.S.A. (*Signed by*) Marston Taylor Bogert, Raymond F. Bacon, Chas. Baskerville.

HART, LESLIE RALPH, 'Beaulieu,' St. Albans, Herts. Research Student. London University B.Sc. Examination in Honours Chemistry, 1st Class, November 1921. (*Signed by*) Samuel Smiles, A. J. Allmand, A. Fairbourne, D. T. Gibson.

HUME-ROTHERY, WILLIAM, Mendip House, Headington Hill, Oxford Research Student in Chemistry. I am a Natural Science Demy of Magdalen College, Oxford, and have taken the Oxford B.A. Degree in Chemistry (Part I of the Final Honours Course) and am now engaged in Research Work in Inorganic Chemistry (for Part II of the Final Honours Course). I intend to devote my life to Research Work and wish to join the Society to keep in touch with the developments of the Science. (*Signed by*) Frederick Soddy, B. Lambert, M. P. Applebey, A. F. Walden, W. H. Perkin, E. Hope.

IRVINE, FRANK MOUAT, 30, Clayton Road, Jesmond, Newcastle-on-Tyne. Lecturer in Chemistry at Armstrong College, Newcastle. B.Sc. (1st Class Hons. Chemistry) (Dunelm), A.I.C. Formerly Research Chemist with Messrs. Cookson & Co., Ltd., Lead and Antimony Manufacturers, Willington, Quay-on-Tyne. (*Signed by*) W. N. Haworth, Grace C. Leitch, J. A. Smythe, C. F. Allpress.

JENKINSON, JOHN ALBERT, School House, Little Sutton, nr. Birkenhead. Science Master at the Plympton Grammar School, South Devon. Student at Liverpool University (Final Examination 1921). B.Sc. (Hons. Chem.). Teacher of Science at Plympton Grammar School. (*Signed by*) E. C. C. Baly, W. C. McC. Lewis, I. M. Heilbron.

JOHNSON, ROWLAND NICHOLAS, 'Greenstede,' West Hill, East Grinstead, Sussex. Research Student at King's College, London. Honours B.Sc. (London), November 1921. First Class in Chemistry with Physics. (*Signed by*) A. J. Allmand, Samuel Smiles, A. Fairbourne.

KOHLI, SARAL JANG, M.Sc., Sat Updesh, Lahore (Punjab), India. Professor of Chemistry, Prince of Wales College (Kashmir State College), Jammu (Kashmir), India. (1) A First Class B.Sc. of the Punjab University, standing first in my combination (Physics and Chemistry) of subjects. (2) A First Class M.Sc. in Chemistry, standing first in the Punjab University. (3) Have done some work on the Radioactivity of Indian Minerals. (4) Have great desire to continue my studies and research work. (5) Am working as a Professor of Chemistry, teaching B.Sc. classes. (*Signed by*) N. A. Yajnik, E. T. Dean, S. R. Khosla.

LAKE, DAVID JOHN, 36, Gerald St., Hafod, Swansea. Science Master, Daventry Grammar School. Passed B.Sc. (London), 1920. Student Swansea Technical College, 1916-1920; Student Swansea University, 1920-Jan. 1921; since Jan. 1921, Science Master, Daventry Grammar School, Northants. (*Signed by*) E. A. Tyler, T. H. Hooper, D. G. Hopkins.

LANGWELL, HUBERT, Wentworth, Denham Road, Epsom, Surrey. Research Chemist. Ten years research on the fermentation of celluloses. (*Signed by*) C. F. Cross, Robt. Ensoll, E. J. Charlton, William Bacon.

Legg, Vernon Howes, 95, Carter Knowle Road, Sheffield. Student, Sheffield University. Took the three years' day course in Chemistry at Sheffield University and obtained the B.Sc. Honours Degree (Chemistry). Am at present engaged in Research Work at the Applied Science Dept. (*Signed by*) W. P. Wynne, R. V. Wheeler, J. Kenner, Arthur W. Chapman.

McRae, John Alexander, Queen's University, Kingston, Ont., Canada. Assistant Professor of Chemistry, Queen's University. M.A. (Queen's Univ., Kingston), Ph.D. (Manchester), F.I.C. 1912–1915, Lecturer on Chemistry, Queen's University, Kingston, Canada. 1915–1919, Asst. Professor of Chemistry, Queen's University, Kingston, Canada. 1919–1921, Research Student at Univ. of Manchester as holder of Special Fellowship from the Honorary Advisory Council for Scientific and Industrial Research of Canada. (*Signed by*) Arthur Lapworth, F. P. Burt, Henry Stephen, F. Fairbrother, Frederick Challenger.

Matthews, Marcus Aurelius, 'Burghley,' 47, Sprattball Rd., Wanstead, E.11. Student for M.Sc. Student at East London College for three years. B.Sc., Second Class Honours in Chemistry. (*Signed by*) F. G. Pope, F. W. Turner, J. R. Partington.

Maxted, Durban Roy, 7, New Road, Reading. Lecturer, University College, Reading. A.R.C.Sc. (1918); B.Sc. (London). 1st Class Hons, Chemistry, 1919. Assistant chemist to Bow Bridge Dye Works, London, E., June 1919–Jan. 1920. Lecturer in Organic Chemistry, University College, Reading, since Feb. 1920. (*Signed by*) H. Bassett, Reginald G. Durrant, J. W. Dodgson.

Morgan, Walter Thomas James, 171, Kensington Avenue, Manor Park, London, E.12. Student, East London College (University of London), Entering for B.Sc. (Hons. Chem.) in Oct. 1922. Inter. B.Sc., 1920. Assistant chemist in the Research Laboratory of the South Metropolitan Gas Company from June 1917–Oct. 1918. (*Signed by*) E. V. Evans, J. R. Partington, F. G. Pope.

Morrison, John Sydney, 23, Seymour Rd., Cheadle Hulme, Manchester. Technical Chemist and English Representative of Messrs. Perry & Hope, Ltd., Firth and Clyde Chemical Works, Nitshill, nr. Glasgow. 1908–1913, Manc. School of Technology, awarded diploma for pure and applied chemistry, also courses in gas engineering, gas manufacturing, bleaching and dyeing, dairy analysis. Ministry of Munitions, D.E.S., London, 1916–1919. Superintendent Chemist and Assistant Manager at Folly explosive gas factories, Gretna, Litherland, West Gorton, and Sutton Oak. Awarded O.B.E. July 1920. Messrs. Perry & Hope, Ltd., Glasgow, 1920–1921, Technical Chemist and Representative. (*Signed by*) James Booth, Herbert H. H. Lorenz, John H. Jeffery, John Turnbull.

Owen, Edward John, Porthdafarch Farm, Holyhead, N. Wales. Organic Chemist, employed by Messrs. The British Drug Houses, Ltd., City Road, London, N.1, in the manufacture of complex organic compounds since Oct. 3, 1921. B.Sc. (Wales) with Second Class Honours in Chemistry. (*Signed by*) Kennedy Orton, Owen Owen, L. Hunter, H. B. Watson, Frederick Soper.

Parsons, Alfred Tennyson, 25, Westwell Rd., Streatham, S.W.16. Chemist, Class 2, Government Laboratory. B.Sc. (Dunelm), A.I.C. (*Signed by*) Robert Robertson, Geo. Stubbs, J. Carmichael.

Patterson, William Hamilton, University of London Club, 21, Gower St., [illegible]C.1. Lecturer in Chemistry, East London College, University of London, [illegible] University of Manchester, A.I.C. Assistant Versuchsanstalt, [illegible]he, Germany. Carnegie Research Scholar, Iron and Steel Institute,

1913. Various Research Publications. (*Signed by*) F. G. Pope, O. L. Brady, W. E. Garner.

PODD, PARTRIDGE LESLIE, 8, St. Peter's St., Ipswich. Post-graduate Research Student at University College, London. Passed B.Sc. Honours Exam. of London University, 1921. As a research student, I desire to have the privilege of using the library of the Society, and I also desire to keep in touch with the advance in knowledge of all branches of chemistry through the medium of the Chemical Society. (*Signed by*) Irvine Masson, Henry Terrey, J. N. E. Day.

RAU, KRISHNARAJPET VENKATA, Ananda College, Colombo, Ceylon. Assistant Master, Ananda College. B.A. (Madras), B.Sc. (London). Ten years' teaching experience. (*Signed by*) J. P. C. Chandrasena, W. N. Rae, M. Parthasarathy.

RAY, FRANK CRAFER, 47, Alfriston Rd., West Side, Clapham Common, S.W.11. Assistant Lecturer, Chemical Department, Battersea Polytechnic, S.W.11. B.A. (Cantab.) (*Signed by*) Harold Hunter, A. Houssa, S. Greenberg, J. L. White, Robert H. Pickard, J. Kenyon.

STEVENSON, FRANCIS MALCOLM, 26, Albert St., Belper, nr. Derby. Dyers' Chemist. Graduated at Leeds University in Colour Chemistry (Hons.), and now desirous of keeping in touch with chemical advances and research. *Signed by*) A. G. Perkin, R. B. Forster, J. B. Cohen.

STEWART, JESSIE, School House, Helmington Row, Crook, Co. Durham. Research Student. B.Sc. Durham University. First Class Honours in Chemistry. (*Signed by*) Samuel Smiles, A. J. Allmand, David T. Gibson.

TATNER, GILBERT HENRY, 52, Melrose Street, Hull. Student, University of Leeds. Studying for Honours B.Sc. (Chemistry). Date of Honours Examination, 1922. (*Signed by*) Arthur Smithells, J. B. Cohen, H. M. Dawson, M. Sybil Leslie, W. Lowson.

TANSLEY, LEONARD BEAUMONT, M.C., M.A., 'Espérance,' Purley, Surrey. Science Coach. Honours Graduate in Chemistry, etc., of Trinity College, Cambridge University. Lecturer and Examination Coach in Science at the General Engineering College, S.W.5. (*Signed by*) Francis Arnall, Frank Matthews, J. C. Crocker.

TAYLOR, GEORGE, *Frigorifico, Campana, F.C.C.A., Argentine, S. America.* Chief Chemist. Member of British Assn. of Chemists. Late Asst. Chemist to Liverpool Gas Co. (*Signed by*) Harold A. Auden, Frank B. Small, J. C Frodsham.

THOMSON, ROBERT WILLIAM MURRAY, 117, Highbury Hill, London, N.5 Lecturer. B.Sc. of St. Andrews University. Assistant Lecturer in Physica Chemistry at King's College, University of London. (*Signed by*) Samue Smiles, H. W. Cremer, John H. Foulger.

WALMSLEY, JAMES RAWSON, Dean Brook Cottage, Dean Lane, Moston Manchester. Analyst and Pharmaceutical Chemist. Member of th Pharmaceutical Society of Gt. Britain. Associate of the Institute o Chemistry. Associate of the Manc. College of Technology (Genl. Chemica Technology). Lecturer (part-time) College of Technology, Manc. (*Signe by*) Frederick Owen, Samuel E. Hodgkinson, Walter Salmon, William Jackso Lund, Jas. Grant.

WHITE, WALTER ARTHUR, 144, Shelley Avenue, Manor Park, E.1 Assistant Analytical Chemist. Assistant to Dr. G. W. Clough in his analytic practice at the Royal Veterinary College, Camden Town. Formerly assista to Dr. G. D. Lander. Student at the Sir John Cass Institute for the Fin B.Sc. (Honours Chemistry) Examination of the University of Londo (*Signed by*) G. W. Clough, W. H. Barker, E. D. Griffiths, W. T. Clough.

WIGHTMAN, WILLIAM PERSEHOUSE DELISLE, 59, Holmewood Gardens, Streatham Hill, London, S.W.2. Student. Student for degree in Chemistry. (*Signed by*) James C. Philip, M. A. Whiteley, H. F. Harwood, H. Ellingham.

WISEMAN, JULIUS, B.Sc., 102, Cambridge Rd., Mile End, E.1. Demonstrator Chemistry Dept., Guy's Hospital, and Student in Medicine. (*Signed by*) C. S. Gibson, A. J. Allmand, Samuel Smiles.

WOOSLEY, DUNCAN PAX, 96, Roxborough Road, Harrow, Middlesex. Chemical Laboratory Assistant. With The British Drug Houses, Ltd., Graham St., City Rd., N.1., since Aug. 1919. Student at Birkbeck College Univ. of London, Sept. 1919 to date, reading for B.Sc. Hons. Chem. I desire to have access to the Library and to keep in touch with modern developments. (*Signed by*) Francis H. Carr, O. A. Le Beau, James Taylor.

WRIGHT, ROBERT NORMAN, 16, Redcliffe St., South Kensington, S.W.10. Assistant Chemist to the Dried Milk Dairy Products Company, Hemyock, Devon. A.R.C.S. (1st Class in Chemistry), B.Sc. (Lond.). (1st class Honours), A.I C. Dec. 1920, appointed assistant chemist in the Research Laboratory of Messrs. J. Lyons & Co., Ltd. (*Signed by*) H. B. Baker, James C. Philip, A. E. Dunstan, F. B. Thole, Philip C. Bull.

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Certificates have been accepted by the Council under Bye-Law I (2) in favour of the following :

BEARPARK, ARTHUR FREDERICK, 'Kingsfold,' Mill Street, Capetown. Postal Address, P.O. Box 1159, Capetown. Postal address in U.K. c/o Henry Tyrer & Co., Ltd., 360, Royal Liver Building, Liverpool. General Manager, Whaling Companies. Three years pupil with H. Thompson, Esq., F.C.S., Hull. Five years chemist to British Oil and Cake Mills, Limited. Member of the Royal Society of South Africa. Member of the South African Chemical Institute. Member of the Chemical, Metallurgical and Mining Society of South Africa. (*Signed by*) Harry Thompson, *Edward B. Maxted.*

SEN, SURESH CHANDRA, Mungpoo P.O., Riyang D. H. Ry., India. Assistant Quinologist, Government of Bengal. B.Sc. (Calcutta), B.A. (Cantab.). Desires to receive the Journal. (*Signed by*) G. E. Shaw.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

*Ordinary Scientific Meeting*, Thursday, February 2nd, 1922, a 8 p.m., Professor H. E. ARMSTRONG, LL.D., F.R.S., Vice-President in the Chair.

The Chairman referred to the loss sustained by the Society through death, of the following Fellows :

| | Elected. | Died. |
|---|---|---|
| Thomas Duxbury | Dec. 15th, 1892. | Nov. 26th, 1921. |
| James Hill Fairweather | June 18th, 1908. | |
| Herbert Garland | May 15th, 1913. | April, 1921. |
| David Emrys Williams | Dec. 6th, 1917. | Jan. 9th, 1922. |

The following were formally admitted Fellows of the Chemica Society: H. C. Bell, S. F. Birch, W. A. P. Challenor, P. ( Chaumeton, L. G. F. Dolley, D. T. Gibson, E. J. Hartung, D. N Jackman, J. H. Middleditch, J. R. Pickering, E. H. Usherwood I. W. Wark, and L. D. Williams.

Certificates were read for the first time in favour of :

George Macdonald Bennett, M.A., M.Sc., F.I.C., 94, Mercers Road, Tufne Park, N.19.
Eric Sykes Brooks, Verandah Buildings, Dalton-in-Furness, Lancs.
Fred Brumfitt, 123, Tennyson Place, Bradford.
Carlton Butler, B.Sc., A.I.C., 23, Winifred Road, Urmston, Manchester.
Francis Arthur Freeth, O.B.E., M.Sc., F.I.C., Heather Croft, Hartford.
Thomas Weatherill Harrison, B.Sc., F.I.C., 18, Elfindale Road, S.E.24.
Eusebius Holmes, B.Sc., Eastern Green, Coventry.
Lingaiah Basavalingaiah Manjunath, B.A., University College, Gower Stree W.C.2.
George Flaxman Underhay, B.Sc., Allerton, Woodside Avenue, Muswe Hill, N.10.
William Andrew Shakespeare Vardy, Winksley Vicarage, Ripon.

A Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of:

Suresh Chandra Sen, B.A., B.Sc., Mungpoo P.O., Riyang, D.H.Ry., India.

*The following papers were read :*

"The action of light on silver bromide." By E. J. HARTUNG.

"The structure of the benzene nucleus. Part I. Intra-nuclear tautomerism." By C. K. INGOLD.

"The structure of the benzene nucleus. Part II. Synthetic formation of the bridged modification of the nucleus." By C. K. INGOLD.

"The structure of the benzene nucleus. Part III. The suppression of intra-nuclear change." By C. K. INGOLD and H. A. PIGGOTT.

"Platinum catalyst for automatic gas lighters." By L. D. WILLIAMS.

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Ordinary Scientific Meeting, held in the Lecture Hall of the Institution of Mechanical Engineers, on Thursday, February 9th, 1922, at 8 p.m., SIR JAMES WALKER, D.Sc., LL.D., F.R.S., President, in the Chair.

SIR ERNEST RUTHERFORD, D.Sc., F.R.S., delivered his Lecture entitled "Artificial Disintegration of Elements." A vote of thanks to the Lecturer, proposed by Professor H. E. Armstrong, seconded by Professor F. G. Donnan, and supported by the Chairman, was carried with acclamation, and acknowledged by Sir Ernest Rutherford.

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Ordinary Scientific Meeting, Thursday, February 16th, 1922, at 8 p.m., SIR JAMES WALKER, D.Sc., LL.D., F.R.S., President, in the Chair.

The PRESIDENT announced that the Society had lost, through death, the following Fellows :

| | Elected. | Died. |
|---|---|---|
| Charles Baskerville ........................... | April 21st, 1898 | Jan. 28th, 1922 |
| George Gilbert Pond ..................... | April 22nd, 1903 | May 20th, 1920 |

The following were formally admitted Fellows of the Chemical Society: A. N. Campbell, W. Davies, A. A. Davis, F. Dickens, A. S. Russell, P. M. Tookey, and M. Williams.

Certificates were read for the first time in favour of:

Frederick Mason Brewer, Lincoln College, Oxford.

Alfred Duncan Gay, 49, Thornlaw Road, West Norwood, S.E.27.

Douglas Cecil Henry, M.A., Hulme Hall, Victoria Park, Manchester.

William Hurst, 2, Edditch Grove, Tonge, Bolton.
Thomas Iredale, B.Sc., 94, Tyrwhitt Road, Brockley, S.E.4.
George Lewis Kennaby, B.Sc., Anglo-Persian Oil Co., Abadan, Persian Gulf.
George Allan Russell, B.Sc., A.I.C., Barnsheen, Ditton, Widnes.
Ernest Arthur Seeley, B.Sc., 10, Hamilton Road, N.5.
Brian Duncan Shaw, Ferns' Hollow, Station Road, Ilkeston.
Arthur Frederick Watson, M.Sc., A.I.C., Brockwell Hall, Herne Hill, S.E.23.
Llywelyn Williams, B.Sc., Herne Bay College, Kent.

*The following Certificate has been authorised by the Council* for presentation to ballot under Bye-Law I (2) in favour of:

Walter Albert Lawrance, M.A., Ph.D., Bates College, Lewiston, Maine, U.S.A.

Messrs. R. Whytlaw Gray and F. G. Pope were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Jnanendra Kumar Adhya, M.Sc.
Harry Charles Applebee, A.I.C.
Gilbert James Avey.
John William Baker, B.Sc.
Bhagwan Das Batta, B.Sc.
Arthur Frederick Bearpark.
Darrell Webb Beesley, A.I.C.
William Alfred Bishop, B.A.
Charles William Brisley, B.A.
Katharine Alice Burke, B.Sc.
Leslie James Burrage, B.Sc.
John Edward Byles, B.Sc., A.I.C.
Reginald Child.
George Hallatt Christie, M.Sc.
Gabriel Cofman-Nicoresti.
William Barry Courtney, B.Sc.
Bernard William Alfred Crutchlow.
Archibald Neil Currie, M.A., B.Sc., A.I.C.
James Owen Cheshyre Dalton, B.A.
Arthur William Edwards.
Samuel Ellingworth, M.Sc.
Kenneth Fisher, M.A., Ph.D.
William Alexander Frederikse.
Miri Lal Goel, M.Sc.
Frank Robert Goss, B.Sc.
Egerton Charles Grey, D.Sc., M.B.
Robert Charles Grimwood.
George Grimshaw Hammond, B.Sc.
William Allen Hamor, M.A.
Leslie Ralph Hart, B.Sc.
William Hume-Rothery, B.A.
Frank Mouat Irvine, B.Sc., A.I.C.
John Albert Jenkinson, B.Sc.
Rowland Nicholas Johnson, B.Sc.
Saral Jang Kohli, M.Sc.
David John Lake, B.Sc.
Hubert Langwell.
Vernon Howes Legg, B.Sc.
John Alexander McRae, M.A., Ph.D., F.I.C.
Marcus Aurelius Matthews, B.Sc.
Durban Roy Maxted, B.Sc.
Walter Thomas James Morgan.
John Sydney Morrison.
Edward John Owen, B.Sc.
Alfred Tennyson Parsons, B.Sc., A.I.C.
William Hamilton Patterson, M.Sc., A.I.C.
Partridge Leslie Podd, B.Sc.
Krishnarajpet Venkata Rau, B.A., B.Sc.
Frank Crafer Ray, B.A.
Suresh Chandra Sen, B.A., B.Sc.
Francis Malcolm Stevenson, B.Sc.
Jessie Stewart, B.Sc.
Gilbert Henry Tatner.
Leonard Beaumont Tansley, M.A.
George Taylor.
Robert William Murray Thomson, B.Sc.
James Rawson Walmsley, A.I.C.
Walter Arthur White.
William Persehouse Delisle Wightman.
Julius Wiseman, B.Sc.
Duncan Pax Woosley.
Robert Norman Wright, B.Sc., A.I.C.

The following papers were read :

"A theoretical derivation of the principle of induced alternate polarities." By A. LAPWORTH.

"An explanation of the property of induced polarity of atoms and an interpretation of the theory of partial valencies on an electronic basis." By W. O. KERMACK and R. ROBINSON.

"Some reactions of benzanthrone." By A. G. PERKIN and G. D. SPENCER.

"A rapid iodimetric estimation of copper and iron in mixtures of their salts." By I. W. WARK.

## ANNUAL GENERAL MEETING.

The Annual General Meeting will take place on Thursday, March 30th, at 4.30 p.m. An Informal Meeting will be held the same evening at 8 p.m.

## REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY.

*(Issued by the Society of Chemical Industry.)*

The Society of Chemical Industry has generously offered to supply Volume VI of these Reports to Fellows of the Chemical Society, who are not Members of the Society of Chemical Industry, at the reduced price of 10/-, post free.

Orders, with remittance, should be sent to Dr. J. P. Longstaff, Secretary, Society of Chemical Industry, 46 and 47, Finsbury Square, London, E.C. 2.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

KINGZETT, CHARLES THOMAS. The popular chemical dictionary. 2nd edition. London 1921. pp. viii + 540. (*Reference.*) 21*s.* net. From the Author.

RUSSELL, T. H. The planning and fitting-up of chemical and physical laboratories. London 1903. pp. xx + 178. ill. (Second Copy.) (*Recd.* 10/1/22.) From the Author.

### II. *By Purchase.*

CHAMOT, ÉMILE MONNIN. Elementary chemical microscopy. 2nd edition. New York 1921. pp. xvi + 480. ill. 25*s.* net. (*Recd.* 21/1/22.)

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, March 2nd, 1922, at 8 p.m., Dr. M. O. Forster, F.R.S., Treasurer, in the Chair.

It was announced that the Society had lost, through death, the following Fellows:

| | Elected. | Died. |
|---|---|---|
| James Robert Appleyard................. | May 15th, 1890. | Oct. 1921. |
| Thomas Lynton Briggs ................. | April 19th, 1883. | April 3rd, 1921. |
| Edward William Taylor Jones ......... | April 6th, 1871. | Feb. 19th, 1922. |

The following were formally admitted Fellows of the Chemical Society: F. B. Arnold, J. W. Baker, A. W. Edwards, F. R. Goss, H. Hunter, W. H. Patterson, F. C. Ray, and S. P. Schotz.

The following List of Nominations for vacant places on the Council, the names of those nominated by the Council being indicated by an asterisk, was read from the Chair:

*Vice-Presidents who have filled the office of President* (*two vacancies*).—*H. B. Dixon; *P. F. Frankland.

*Vice-Presidents who have not filled the office of President* (*two vacancies*).—*E. C. C. Baly; *T. M. Lowry.

*Secretary* (*one vacancy*).—*Irvine Masson.

*Ordinary Members of Council:* (*a*) Town Members, that is, those resident within 50 miles of Charing Cross (three vacancies).—C. Dorée; J. J. Fox; J. R. Partington. (*b*) Country Members, that is, those resident beyond 50 miles from Charing Cross (three vacancies).—*I. M. Heilbron; J. W. McBain; *W. H. Mills.

Certificates were read for the first time in favour of:

**Brojo Kishore Banerjee, B.Sc., Jamshedpur Technical Institute, Tatanagar, India.**

**Benoy Bhusan Basu, B.Sc., M.B., 1/1, Nepal Bhattacherji's Street, Kalighat P.O., Calcutta.**

Leslie Ashburn Dunn, 9, Pembroke Terrace, Bridlington.
Richard Fisher, Hudshaw House, Hexham, Northumberland.
Herbert Hodgson, 35, Ryan Street, Bradford.
Arthur Cyril Percy Lunn, King's College, Cambridge.
Robert Craig McDowall, 6, Ascog Street, Crosshill, Glasgow.
Akella Suryanarayana Rao, B.Sc., Vizagapatam, India.
Harry Lister Riley, 7, Trafalgar Square, Chelsea, S.W.3.
James Robinson, B.Sc., Milton High School, Bulawayo, S. Rhodesia.
Suhramania Sastry, B.A., 5, Krishnappa Naik Agraharam, Georgetown, Madras.

The following papers were read:

"New halogen derivatives of camphor. Part II. α′-Bromocamphor." By T. M. Lowry, V. Steele, and H. Burgess.

"The rotatory dispersive power of organic compounds. Part X. The preparation and properties of pure ethyl tartrate." By T. M. Lowry and J. O. Cutter.

"The molecular configuration of polynuclear aromatic compounds. Part I. The resolution of γ-6 : 6′-dinitro- and 4 : 6 : 4′ : 6′-tetranitrodiphenic acids into optically active components." By G. H. Christie and J. Kenner.

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Ordinary Scientific Meeting, Thursday, March 16th, 1922, at 8 p.m., Sir James Walker, D.Sc., F.R.S., President, in the Chair.

A. T. Parsons was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

John William Blagden, M.A., Ph.D., F.I.C., Apple Tree House, Grove Road, Woodford, E.18.
Charlie Lyons Carter, M.Sc., 9, Carr Street, N.E. Valley, Dunedin, N.Z.
Arthur Rockett Chadwick, Corporation Sewage Works, Marley, Keighley.
Douglas Creese Harrison, B.Sc., 18, Church Crescent, Muswell Hill, N. 10.
Henry Unwin Harrow, 13, Southwark Bridge Road, S.E. 1.
Ethel Mary James, B.Sc., 1, Rusham Road, Balham, S.W. 12.
Edward Ingleson Lawson, 65, Warrington Road, Newcastle-on-Tyne.
*John Mylne Mullaly, 14, Bardwell Road, Oxford.*
Harold Edward Charles Powers, B.Sc., 4, Grove Crescent, Woodford, E. 18.
Albert W. Smith, B.S., Ph.D., Case School of Applied Science, Cleveland, Ohio, U.S.A.
Clarence Stott, B.Sc., A.I.C., Benroyd, Holywell Green, Halifax.
William Thomas, B.A., M.Sc., A.I.C., Penfro, Stoneywood, Aberdeen.
John George Walters, B.Sc., 46, Durham Road, East Finchley, N. 2.
William Wallace Watt, 29, Woodstock Road, Golders Green, N.W. 4.
Harry Alexander Wood, Santa Elena, Entre Rios, Argentine.

The following Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2):

Harilal Basu, P.O. Box 84, Rangoon, Burma.

The following papers were read:

"Change of properties of substances on drying." By H. B. BAKER.

"The influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Part VI. The elimination of halogen during the reduction of halogenated nitro-compounds." By H. BURTON and J. KENNER.

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## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

DUDLEY, DUD, and others. Mettallum Martis: or iron made with pit-coale, sea-coale, etc., 1665. A treatise of metallica. By JOHN ROVENZON, 1613. Metallica, or the treatise of metallica. By SIMON STURTEVANT, 1612. [Edited by JOHN N. BAGNALL. Wolverhampton 1854.] pp. xix + 43, ii + 30, ii + 120. ill. (*Reference.*) From Professor P. Phillips Bedson.

FISCHER, EMIL. Aus meinem Leben. Berlin 1922. pp. vi + 202. ill. (*Recd.* 18/2/22.) From the Publisher: Julius Springer.

HADFIELD, SIR ROBERT ABBOTT. The work and position of the metallurgical chemist, also references to Sheffield and its place in metallurgy. An address. [London 1921.] pp. 97. ill. (*Recd.* 2/3/22.) From the Author.

HILDITCH, THOMAS PERCY. A concise history of chemistry. 2nd edition. London [1922]. pp. xii + 276. 6*s*. net. (*Recd.* 24/2/22.) From the Publishers: Messrs. Methuen & Co.

JOHNSTONE, SYDNEY JAMES. Potash. (Imperial Institute Monograph on Mineral Resources.) New edition. London 1922. pp. x + 122. 6*s*. net. (*Recd.* 2/3/22.) From the Director.

KANTHACK, R. (Compiler.) Tables of refractive indices. Vol. II. Oils, fats, and waxes. Edited by JOHN NAISH GOLDSMITH. London 1921. pp. 296. 25*s*. net. (*Recd.* 3/3/22.)

From the Publishers: Messrs. Adam Hilger Ltd.

MINISTRY OF MUNITIONS and DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. Technical records of explosives supply 1915–1918. No. V. Manufacture of sulphuric acid by contact process. London 1921. pp. vi + 128. ill. 25*s*. net. (*Recd.* 3/3/22.)

—— —— No. VI. Synthetic phenol and picric acid. London 1921. pp. vi + 98. ill. 15*s*. net. (*Recd.* 14/2/22.)

*From the Department.*

PAULI, WOLFGANG. Colloid chemistry of the proteins. Part I. Translated by PERCY CYRIL LESLEY THORNE. London 1922. pp. xii + 140. ill. 8*s*. 6*d*. net. (*Recd.* 28/2/22.)

From the Publishers: Messrs. J. & A. Churchill.

II. *By Purchase.*

ARCHIVIO DI FARMACOLOGIA SPERIMENTALE E SCIENZE AFFINI. Year *XVIII*, *Vol. XXVII*, etc. Siena *1919* +. (*Reference.*)

BAUER, K. H. Analytische Chemie der Alkaloide. Berlin 1921. pp. vi + 425. ill. (*Recd.* 18/2/22.)

BEILBY, SIR GEORGE. Aggregation and flow of solids: being the records of an experimental study of the micro-structure and physical properties of solids in various states of aggregation. 1900–1921. London 1921. pp. xvi + 256. + xxxiv plates. 20*s*. net. (*Recd.* 21/2/22.)

CHEMIKER-KALENDER 1922. Edited by WALTHER ROTH. Year 34. 2 vols. Berlin 1922. (*Reference.*)

DEERR, NOËL. Cane sugar: a textbook on the agriculture of the sugar cane, the manufacture of cane sugar, and the analysis of sugar-house products. 2nd edition. London 1921. pp. viii + 644. ill. 42*s*. net. (*Recd.* 17/1/22.)

FOERSTER, FRITZ. Elektrochemie wässeriger Lösungen. 3rd edition. Leipzig 1922. pp. xx + 900. ill. (*Recd.* 18/2/22.)

FORTSCHRITTE IN DER ANORGANISCH-CHEMISCHEN INDUSTRIE: an Hand der Deutschen Reichs-Patente dargestellt. Edited by ADOLF BRÄUER and JOHANNES D'ANS. Vol. I, 1877–1917, etc. Berlin 1921 +. ill. (*Reference.*)

GATTEFOSSÉ, R. M., and GATTEFOSSÉ, J. Nouveaux parfums synthétiques. Lyon 1921. pp. 208. ill. 5*s*. 6*d*. net. (*Recd.* 6/2/22.)

GOW, COLIN CLARENCE. The electro-metallurgy of steel. London 1921. pp. xvi + 351. ill. 27*s*. 6*d*. net. (*Recd.* 17/1/22.)

GRASSER, GEORG. Synthetic tannins: their synthesis, industrial production, and application. Translated by FINI G. A. ENNA. London 1922. pp. viii + 143. 12*s*. net. (*Recd.* 17/1/22.)

HIGGINS, SYDNEY HERBERT. Bleaching: being a résumé of the important researches on the industry published during the years 1908—1920. Manchester 1921. pp. viii + 138. 10*s*. 6*d*. net. (*Recd.* 21/1/22.)

HIRSCH, PAUL. Die Einwirkung von Mikroorganismen auf die Eiweisskörper. (Biochemie in Einzeldarstellungen. IV.) Berlin 1918. pp. x + 256. ill. (*Recd.* 3/3/22.)

HÖFER, JOHANNES. Die Fabrikation künstlicher plastischer Massen sowie der künstlichen Steine, Kunststeine, Stein- und Zementgüsse. 4th edition. Wien 1921. pp. xii + 366. ill. (*Recd.* 25/1/22.)

ILLINGWORTH, STEWART ROY, assisted by JENKYN GRIFFITHS. The analysis of coal and its by-products. London [1921]. pp. [xii] + 380. ill. 21*s*. net. (*Recd.* 17/1/22.)

KANITZ, ARISTIDES. Temperatur und Lebensvorgänge. (Biochemie in Einzeldarstellungen. I.) Berlin 1915. pp. x + 175. ill. (*Recd.* 3/3/22.)

KAUFFMANN, HUGO. Beziehungen zwischen physikalischen Eigenschaften und chemischer Konstitution. (Chemie in Einzeldarstellungen, Vol. X.) Stuttgart 1920. pp. xii + 422. (*Recd.* 13/2/22.)

KLIMONT, I. M. Der technisch-synthetische Campher. (Chem. Tech. in Einzeldarstellungen.) Leipzig 1921. pp. viii + 132. ill. (*Recd.* 3/3/22.)

KOLTHOFF, I. M. Der Gebrauch von Farbenindicatoren. Ihre Anwendung in der Neutralisationsanalyse und bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration. Berlin 1921. pp. iv + 144. ill. (*Recd.* 3/3/22.)

ORGANIC SYNTHESES. An annual publication of satisfactory methods for the preparation of organic chemicals. Edited by ROGER ADAMS, JAMES BRYANT CONANT, HANS THACHER CLARKE, and OLIVER KAMM. Vol. I, etc. New York 1921 +. ill. (*Reference.*) 8*s*. 6*d*. net.

PRINGSHEIM, PETER. Fluoreszenz und Phosphoreszenz im Lichte der neueren Atomtheorie. Berlin 1921. pp. viii + 202. ill. (*Recd.* 13/2/22.)

RICHTER, VICTOR VON. Organic chemistry, or chemistry of the carbon compounds. Edited by RICHARD ANSCHÜTZ and HANS MEERWEIN. II. Carbocyclic compounds. Translated from the 11th German edition by EDMUND EDWARD FOURNIER D'ALBE. London 1922. pp. xvi + 760. (*Reference.*) 35*s*. net.

RÖHMANN, FRANZ. Über künstliche Ernährung und Vitamine. Biochemie in Einzeldarstellungen. II.) Berlin 1916. pp. vi + 150. ill. (*Recd.* 3/3/22.)

SIEGFRIED, MAX. Über partielle Eiweisshydrolyse. (Biochemie n Einzeldarstellungen. III.) Berlin 1916. pp. iv + 64. (*Recd.* 3/3/22.)

SOCIÉTÉ DE CHIMIE BIOLOGIQUE. Bulletin. Vol. I, etc. Paris 1914 +.

STEPHENSON, CHARLES H. Some micro-chemical tests for alkaoids. Including "Chemical tests of the alkaloids used." By CHARLES EDWIN PARKER. London 1921. pp. iv + 110 + xxvii plates. 21*s*. net. (*Recd.* 17/1/22.)

TAYLOR, HUGH STOTT. Industrial hydrogen. New York 1921. pp. 210. ill. 20*s*. net. (*Recd.* 21/1/22.)

THOMSON, SIR JOSEPH JOHN. Rays of positive electricity and heir application to chemical analyses. 2nd edition. London 1921. pp. x + 238. ill. 16*s*. net. (*Recd.* 21/1/22.)

TREADWELL, FREDERICK PEARSON. Analytical chemistry. Vol. I. Qualitative analysis. 5th English edition. Translated by WILLIAM T. HALL. New York 1921. pp. xviii + 598. ill. 23*s*. net. (*Recd.* 12/1/22.)

## III. *Pamphlets.*

ARRHENIUS, SVANTE. Aus meiner Jugendzeit. Leipzig 1913. pp. 18.

ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS and BRITISH CHEMICAL PLANT MANUFACTURERS' ASSOCIATION. *Joint Research Committee on Chemical Plant.* Report of sub-committee for standardisation of jacketted pans. [London 1922.] pp. 14. ill.

CHEMICAL SOCIETY. Notes on the furnishing and equipment of chemical laboratories. London 1921. pp. 11.

CROMPTON, HOLLAND. Nebular zones and the formation of planets. [London 1921.] pp. 19.

IMPERIAL MINERAL RESOURCES BUREAU. The Mineral Industry of the British Empire and Foreign Countries. War Period. Mica (1913—1919). London 1922. pp. 32.

—— —— Sulphur and iron-pyrites. (1913–1919.) London 1922. pp. 67.

SCIENTIFIC AND INDUSTRIAL RESEARCH, DEPARTMENT OF. *Building Research Board.* Special Report No. 4. The transmission of heat and gases through, and the condensation of moisture on the surface of, wall materials: an extract from the report of the Building Materials Research Committee. London 1921. pp. 19. ill.

SCIENTIFIC AND INDUSTRIAL RESEARCH, DEPARTMENT OF. *Fuel Research Board.* Fuel for motor transport. Second Memorandum. London 1921. pp. iv + 16.

—— —— *Special Report No. 1.* Pulverised coal systems in America. By LEONARD C. HARVEY. Revised edition. London 1922. pp. iv + 117. ill.

SINGH, BAWA KARTAR. Recent advances in stereochemistry. (From the *J. Proc. Asiatic Soc. Bengal*, 1921, N.S. **17**.)

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# CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, MAY 4TH, 1922.

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N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

BANERJEE, BROJO KISHORE, Jamshedpur Technical Institute, G. Town, Jamshedpur, Tatanagar, India. Assistant, Chemical and Analytical Department, Jamshedpur Technical Institute, Tatanagar, India. B.Sc. (Calcutta University). Read up to M.Sc. Chemistry with Inorganic Chemistry as special subject in the post-graduate classes of the Calcutta University. Had been assistant in the Chemical and Metallurgical Dept. of the Bengal Engineering College, Sibpur, India, for two and a half years nearly. Now assistant in the Chemical and Analytical Dept. of the Jamshedpur Technical Institute since August 1921. Lecturing on General Inorganic Chemistry since March 1919. (*Signed by*) R. N. Sen, P. C. Chattopadhyay, J. Bhaduri.

BASU, BENOY BHUSAN, 1/1, Nepal Bhattacherji's Street, Kalighat P.O., Calcutta, India. B.Sc., M.B. Assistant Chemical Analyst to the Calcutta Corporation, intending to keep in touch with the modern advancement in Chemistry and the chemical world. (*Signed by*) B. N. Ghosh, T. K. Ghose, K. B. Sen.

BENNETT, GEORGE MACDONALD, 94, Mercers Road, Tufnell Park, N.19. Demonstrator, Chemical Department, Guy's Hospital Medical School. B.A., M.Sc. (London), M.A. (Cantab.), F.I.C. Fellow of St. John's College, Cambridge. Author of several papers in the Transactions since 1913. (*Signed by*) C. S. Gibson, D. C. Vining, Eustace E. Turner, H. C. Bell.

BLAGDEN, JOHN WILLIAM, Apple Tree House, Grove Road, Woodford, E.18. Head of Research Dept., Messrs. Howards & Sons, Ilford. M.A. (Cantab.), Ph.D. (Würzburg), F.I.C. 1899–1900 Demonstrator at the Electrochemical Institute of the Polytechnic, Darmstadt. 1900–1914 Research Chemist with Messrs. Boehringer & Sons, Mannheim. (1914–1919 Civilian *Prisoner of War at Ruhleben.)* 1919–1922 with Messrs. Howards & Sons as above stated. (*Signed by*) H. B. Baker, J. T. Hewitt, M. O. Forster.

BREWER, FREDERICK MASON, 42, Aberdeen Park, London, N.5. Student. Science Scholar of Lincoln College, Oxford. (*Signed by*) W. H. Perkin, T. W. J. Taylor, *D. Ll. Hammick*, E. Hope, S. G. P. Plant, N. V. Sidgwick.

BROOKS, ERIC SYKES, M.P.S., Verandah Buildings, Dalton-in-Furness,

ancs. Chemist. Member of Pharmaceutical Society of Great Britain. tudent of Chemistry for the past eight years, also as private coach for lementary chemistry. (*Signed by*) Alex. W. McLaren, Chas. Morton, Alfred 'homas.

BRUMFITT, FRED, 123, Tennyson Place, Bradford. Director and Manager, Vholesale Druggists. Diploma Chemistry and Dyeing, Bradford Technical 'ollege. Wholesale Druggist. (*Signed by*) V. Steele, F. W. Richardson, Sarkpr North.

BUTLER, CARLTON, B.Sc., A.I.C., 23, Winifred Road, Urmston, nr. Manhester. Research Student in the Victoria University of Manchester. ,anc. C.C. Scholar 1917. Served Sp. Brig. R.E. until Jan. 1919. First 'lass Honours Chemistry 1921. Research, and part-time demonstrator, ession 1921–22. (*Signed by*) H. B. Dixon, Colin Campbell, Frederick Chalenger, Henry Stephen.

CARTER, CHARLIE LYONS, 9, Carr Street, N.E. Valley, Dunedin. Lecturer n Chemistry, Otago University, Dunedin, New Zealand. M.Sc. with 1st 'lass Honours in Chemistry, N.Z., 1919. A.I.C. (London), 1921. Demontrator in chemistry, Otago University, 1917–19. Lecturer on Chemistry, 919. Publication: "Mutton-bird Oil," *Jour. Soc. Chem. Ind.*, Sept. 1920, . 220. (*Signed by*) J. K. H. Inglis, J. Williams, C. S. Hicks.

CHADWICK, ARTHUR ROCKETT, Corporation Sewage Works, Marley, Keighey. Chemist and Manager, Keighley Corporation Sewage Works. Eighteen nd a half years' experience in the Chemistry of Sewage Disposals. Chemist nd Manager, Keighley Corporation Sewage Works for two years. Chemist nd Manager, Bingley U.D.C. Sewage Works for five years. Chemist and lanager, Prestwich U.D.C. Sewage Works for one and a half years. Chemist nd under-Manager at the Thornhill Sewage Works of the County Borough f Dewsbury for ten years. Eight years student at the Dewsbury Technical chool in Chemistry and Allied Subjects, and hold Board of Education ertificates for all stages. I desire to join your Society so that I can keep in ouch with modern methods of water, sewage and trades-waste purification, o obtain your publications and to have the use of your library. (*Signed by*) ames H. Kershaw, Herbert J. Taylor, John Senior.

DUNN, LESLIE ASHBURN, 9, Pembroke Terrace, Bridlington. Assistant Vorks Chemist, employed by Messrs. Raines & Porter, Ltd., Hull. Was ducated at Bridlington School (by scholarship). Studied Chemistry norganic, organic, and industrial) at Hull Technical College. Served with st E. Yorks. Regt. during the war. Finally assistant to T. A. Nightscales, lsq., F.C.S. (*Signed by*) Thos. A. Nightscales, Harry Thompson, W. Geary.

FISHER, RICHARD, Hudshaw House, Hexham, Northumberland. Student. )uring war I was employed in the Hydrophone Department of the Navy Special Technical Branch). After the war I took up Medical Studies and ave always wished for up-to-date chemical information. (*Signed by*) '. C. Garrett, C. R. Gent, John Gibson.

FREETH, FRANCIS ARTHUR, Heather Croft, Hartford. Chief Chemist, lessrs. Brunner, Mond & Co., Ltd. M.Sc. (Liv.), F.I.C., F.Inst.P., O.B.E. Signed by) F. G. Donnan, W. E. Garner, Henry Terrey, Irvine Masson.

GAY, ALFRED DUNCAN, 49, Thornlaw Road, West Norwood, S.E.27. nalytical Chemist. Three years Junior Assistant to Dr. Bernard Dyer. 'ifteen months Assistant Chemist to The Magadi Soda Co., Ltd., B.E.A. Recently engaged as Analytical Chemist to Schweppes, Ltd., Mineral Water lanufacturers. (*Signed by*) R. Lessing, Bernard Dyer, Wm. H. Woodcock, leorge Taylor.

HARRISON, DOUGLAS CREESE, 18, Church Crescent, Muswell Hill, London, N.10. Research Student in Organic Chemistry under Prof. Smiles at King's College, London. Passed Exam. for B.Sc. (London) with 1st Class Honours, with Chemistry as principal subject and Physics subsidiary. (*Signed by*) Samuel Smiles, A. J. Allmand, A. Fairbourne.

HARRISON, THOMAS WEATHERILL, 18, Elfindale Road, S.E.24. Chemist, Government Laboratory, London. B.Sc. (London). F.I.C. "Titration with Permanganate in Presence of Hydrochloric Acid." "The Action of Dimethyl Sulphate upon Oils of the Aromatic and Aliphatic Series." (*Signed by*) E. Grant Hooper, Geo. Stubbs, J. J. Fox.

HARROW, HENRY UNWIN, 13, Southwark Bridge Road, S.E.1. Senior Assistant Chemist, Barclay, Perkins' Brewery. Inter. B.Sc. (London), 1906. *Chemist, South African Breweries, Johannesburg, from 1913 to 1920.* Sitting for B.Sc. Hons. (London) in 1923 (October). (*Signed by*) J. Kenyon, J. L. White, S. Greenberg.

HENRY, *DOUGLAS CECIL, M.A., Hulme Hall, Victoria Park, Manchester.* Lecturer in Chemistry at the University of Manchester; Fellow of Trinity College, Cambridge; late Coutts-Trotter Scholar. Two years' research work, *not at present published, on Adsorption from Solution, the results embodied* in a thesis; won a Fellowship of Trinity College, Cambridge (Oct. 1921). Teaching experience—two years' coaching and tutorial work for Trinity, *Cambridge. Lecturing and demonstrating at Manchester.* (*Signed by*) Harold B. Dixon, Arthur Lapworth, F. P. Burt, J. E. Myers, Henry Stephen, Angus F. Core, Colin Campbell.

HODGSON, HERBERT, 35, Ryan Street, Bradford, Yorks. Analytical Chemist. Over twenty years assistant to Mr. F. W. Richardson, City Analyst of Bradford, and County Analyst of W.R. of Yorks. Also with the firm of Messrs. Richardson & Jaffé, Industrial Chemists. Experience in most branches of Analytical Chemistry. Also with R.E. "Anti-Gas," University College, London. (*Signed by*) F. W. Richardson, A. Jaffé, Geoffrey A. Bracewell.

HOLMES, EUSEBIUS, Eastern Green, Coventry. Student of Chemistry. Qualified for B.Sc. (Birm.). Desiring access to recent chemical literature. (*Signed by*) C. E. Wood, Wm. Wardlaw, E. Ashley Cooper.

HURST, WILLIAM, 2, Edditch Grove, Tonge, Bolton. Analytical and Manufacturing Chemist, c/o Thos. Moscrop & Co., Bolton, Oil Blenders and Refiners, Lubricants, etc. 1st Class Certificates, Lancs. and Cheshire Inst.: Mathematics 3rd year, and Chemistry, Inorganic and Organic, 4th year. Final Certificate of The City and Guilds Inst., London, in Oils, Fats, and Waxes. Two and a half years' Senior Chemistry Course (full time), Mining and Technical College, Wigan, 1919–1921. At present attending the College of Technology, Manchester. (*Signed by*) John Allan, Frank Lee Pyman, E. B. Naylor, T. H. Winstanley.

IREDALE, THOMAS, 94, Tyrwhitt Road, St. Johns, S.E.4. Scholar of the 1851 Exhibition. B.Sc. (Sydney, Australia), 1919. Have since been engaged in research. Papers published in Transactions of Chem. Soc. (1921). *Signed by*) F. G. Donnan, I. W. Wark, E. J. Hartung, D. C. Jones.

JAMES, ETHEL MARY, 1, Rusham Road, Balham, S.W.12. Assistant Science Mistress, Clapham County Secondary School, S.W.11. B.Sc. (Lond.); Hons. Chem. 1920, after studying at Bedford College from 1916–20. At present teacher of chemistry at the above school. (*Signed by*) Holland Crompton, J. F. Spencer, M. S. Crewdson.

KENNABY, GEORGE LEWIS, Abadan, Persian Gulf. Chemist. B.Sc.

(London), 3rd Class Honours in Chemistry, 1920, since which I have been working for the Anglo-Persian Oil Co. at their refinery in Persia. I am desirous of keeping in touch with the recent developments in chemistry with the object of taking my A.I.C. at some future date. (*Signed by*) F. G. Donnan, W. E. Garner, Irvine Masson, Henry Terrey.

LAWSON, EDWARD INGLESON, 65, Warrington Road, Newcastle-on-Tyne. Teacher of Chemistry at Dame Allan's School, Newcastle-on-Tyne. Student of Chemistry for four years at Leeds University. Teacher of Chemistry for four years at Newcastle. (*Signed by*) J. R. Scott, R. M. Woodman, John Stanley Carter, Edgar Rhodes.

LUNN, ARTHUR CYRIC PERCY, King's College, Cambridge. Student. Part I Nat. Science Tripos, 1921. Taking Part II (Chemistry, May 1922). (*Signed by*) Hamilton McCombie, Harold A. Scarborough, A. E. Cashmore, C. T. Heycock, W. H. Mills, Douglas F. Harrison.

McDOWALL, ROBERT CRAIG, 6, Ascog Street, Crosshill, Glasgow. Analytical Chemist to Messrs. Perry & Hope, Ltd., Forth & Clyde Chemical Works, Nitshill. Cream of Tartar Subs., Malt Extract, Food Products generally 1904–1911 (7 years). Technical and Chemical Adviser to Messrs. Craig, McDowall & Co., Thornliebank, Glasgow, Cream of Tartar Subs., Baking Powders, and other Food Products, Mag. Sulph., Ferro Sulph., Soda Sulph., etc., 1911–1915 (4½ years). Glasgow Highlanders, H.M. Forces, 1915–1918 (3½ years). Technical Chemist and Representative, also Process Superintendent to Messrs. Perry & Hope, Ltd., Forth & Clyde Chemical Works, Nitshill, 1918–1922 (4 years). Having been connected for the past sixteen years with the manufacture and analysis of foodstuffs I am desirous of keeping in touch with all latest books and papers appertaining to same. (*Signed by*) James Booth, J. Turnbull, Herbert Lorenz, W. McHutchison.

MANJUNATH, LINGAIAH BASAVALINGAIAH, London. Student of the London University. B.A. degree in Chemistry of the Madras University. At present a student for the London M.Sc. degree in Chemistry in the University College. (*Signed by*) O. L. Brady, E. H. Thierry, J. N. E. Day.

MULLALY, JOHN MYLNE, 14, Bardwell Road, Oxford. Student of Chemistry. Part author of paper *Trans. Chem. Soc.* CXIX, p. 1802 (1921). Commoner of Balliol College. (*Signed by*) H. Hartley, C. N. Hinshelwood, E. J. Bowen, H. R. Raikes.

POWERS, HAROLD EDWARD CHARLES, 4, Grove Crescent, Woodford, E.18. Analytical Chemist. B.Sc. Hons. (2nd Class). About six years' practical experience in technical laboratory. (*Signed by*) Hugh Main, George Senter, F. Barrow, S. Sugden, Alfred J. White.

RAO, AKELLA SURYANARAYANA (Junior), Vizagapatam, India. B.Sc. in Chemistry, Botany (National University, Adyar, Madras). I intend joining the Society fully believing that by doing so I shall be in the know of the recent work in chemistry, which would be of immense use to me as a prospective research chemist. (*Signed by*) T. S. Natrajan, S. N. Dhar, K. C. Viraraghavan.

RILEY, HARRY LISTER, 7, Trafalgar Square, Chelsea, S.W.3. Student (Research) at the Royal College of Science. A.R.C.Sc. and B.Sc. (Hons.) London. (*Signed by*) H. B. Baker, James C. Philip, J. N. Sugden, H. J. T. Ellingham, A. A. Eldridge.

ROBINSON, JAMES, Bulawayo, S. Rhodesia. Science Master, Milton High School, Bulawayo. B.Sc., Univ. of Wales. Completed 1st year London Final Sc. Course in Mechanical Engineering (Matriculated 1st Div. Inter. Sc., London). Completed advanced practical courses on Fibres, Detergents,

Alkaloids, Assays. One session's research work on "The Action of $SO_2$, Sulphites, Meta-bisulphate on various *Peroxides* ($BaO_2$, $H_2O_2$, $CeO_2$, $PbO_2$) in Comparison with $MnO_2$ and with the action on $K_2Mn_2O_8$,$CrO_3$, and Persulphates as Oxidising Agents," under Prof. Herbert Jackson, King's College, London. (*Signed by*) Geo. A. Pingstone, Arthur Slator, A. L. Stern.

Russell, George Allan, Barnsheen, Ditton, Widnes. Chemist to Messrs. T. Vickers & Sons, Ltd., Phosphate Works, Widnes. B.Sc. (Dun.). A.I.C. Five years' laboratory and works experience with the United Alkali Co., Ltd., Widnes, in the manufacture of monochlorbenzene, chloracetic acid, and concentration of sulphuric acid, and subsequently two and a half years' (to date) experience with Messrs. T. Vickers & Sons, Ltd., Widnes, in the manufacture of sulphuric acid, Fertilisers and Phosphate of Soda, and in the corresponding analytical work. (*Signed by*) F. C. Garrett, J. A. Smythe, P. L. Robinson, John W. Towers, *John Hargreaves*.

Sastry, M. Suhramania, 5, Krishnappa Naik Agraharam, Georgetown, Madras, India. Chemical Assistant, Government Leather Trades Institute, Madras. B.A. (Madras). Post Graduate Course for two and a half years (Madras University). Chemical Assistant. (*Signed by*) Kalyan C. Srinivasan, T. S. Natrajan, K. C. Viraraghavan, *S. N. Dhar*.

Seeley, Ernest Arthur, 10, Hamilton Road, London, N.5. Chemical Research Student. B.Sc. 1st Class Hons. Chem. (Lond.), A.R.C.S. (1st Chem.). D.I.C. (Organic Chemistry Research). (*Signed by*) Jocelyn Thorpe, C. K. Ingold, L. C. Nickolls.

Shaw, Brian Duncan, Ferns' Hollow, Station Road, Ilkeston. Student. Second Year Hon. Chem. Student (for B.Sc. Lond.) at University College, Nottingham. (*Signed by*) F. S. Kipping, F. C. Laxton, G. Green.

Smith, Albert W., Case School of Applied Science, Cleveland, Ohio, U.S.A. Professor of Chemistry. Graduate of Chemical Dept. of Case School of Applied Science (B.S.). University of Zürich, Switzerland (Ph.D.). (*Signed by*) Olin F. Tower, Chas. F. Guhlmann, Chas. H. Herty.

Stott, Clarence, Benroyd, Holywell Green, nr. Halifax. Works Chemist. (*a*) B.Sc. (Leeds); (*b*) A.I.C.; (*c*) Diploma in Gas Engineering (Leeds); (*d*) War Service: Army, 4½ years; B.E.F. France, 3½ years; rank: Capt. The last two years of service overseas were spent in Chemical Warfare as Gas Officer to the 49th (West Riding) Division. Honours: (1) Mentioned in Despatches; (2) Military Cross. (*e*) Works experience: 1¾ years' laboratory and plant experience with the Farnley Iron Co., nr. Leeds. (*Signed by*) John W. Cobb, Arthur Smithells, Herbert Ingle.

Thomas, William, Penfro, Stoneywood, Aberdeen. Lecturer in Chemistry, University, Aberdeen. M.Sc. (Wales). B.A. (Cantab.). A.I.C. (*Signed by*) Alex. Findlay, T. Harold Reade, Edward Bloom.

Underhay, George Flaxman, Allerton, Woodside Avenue, Muswell Hill, N.10. Research at University College, London. 2nd Class Honours B.Sc. (Chemistry). Now engaged on research under Prof. F. G. Donnan, C.B.E., F.R.S., at University College. (*Signed by*) F. G. Donnan, J. N. Collie, Irvine Masson, *O. L. Brady*.

Vardy, William Andrew Shakespeare, Winksley Vicarage, Ripon. Analytical Chemist, relinquished on account of ill-health. Late Student in Science and Member of Ripon G.S. Scientific Society. Analytical Chemist. (*Signed by*) A. Mortimer, Barker North, T. W. Price.

Walters, John George, 46, Durham Road, East Finchley, N.2. Teacher. B.Sc. (London). Senior Chemistry Master, County Secondary School, Hendon, N.W.4. Late Commandant XVII Corps Gas School, B.E.F., and Chemical

Adviser XVII Corps, B.E.F. (*Signed by*) T. J. Drakeley, P. Schidrowitz. Raymond R. Butler.

WATT, WILLIAM WALLACE, 29, Woodstock Road, Golders Green, N.W.4. Consulting Petroleum Technologist. Chief Chemist, Burmah Oil Co., Rangoon (13½ years). Technical Staff (London), Anglo-Persian Oil Co. (1½ years). Deputy Controller of Oil to H.M. Govt. of India (1 year). Technical Advise Caltex Oil Co., London (1½ years). (*Signed by*) F. B. Thole, A. E. Dunstan J. C. Crocker, F. Arnall.

WATSON, ARTHUR FREDERICK, Brockwell Hall, Herne Hill, S.E.23 Research Chemist. University College, London, 1913–15, 1919–21; B.Sc (War) degree, 1917. B.Sc. (Honours Chemistry), 1920. A.I.C. 1921 Research in Biological Chemistry, 1920–1921. M.Sc. (Physiologica Chemistry), 1921, London. (*Signed by*) J. C. Drummond, Irvine Masson F. G. Donnan.

WILLIAMS, LLYWELYN, Herne Bay College, Kent. Assistant Master B.Sc. (*Wales*) *in Chemistry and Physics. My present appointment is tha* of Senior Science and Mathematics Master at Herne Bay College, Kent (*Signed by*) T. Campbell James, C. R. Bury, L. J. Hudleston.

WOOD, HARRY ALEXANDER, Santa Elena, Entre Rios, Argentine Republic Industrial Chemist. (*a*) Analytical Assistant to Prof. James Hendrick, B.Sc. F.I.C., Professor of Agriculture, Aberdeen University (3 years); (*b*) Analytica Assistant to Dr. J. F. Tocher, F.I.C., Public Analyst and Official Agricul tural Analyst (3 years); (*c*) Works Chemist: Establecimientos Argentino de Bovril Santa Elena, Entre Rios, Argentine Republic (1½ years). (*Signe by*) James Hendrick, J. F. Tocher, A. Searl.

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The following Certificates have been authorised by the Council fo presentation to ballot under Bye-law I (2):

BASU, HARILAL, Care of the Inspector-General of Civil Hospitals, Burma Rangoon, Post Box No. 84. Civil Surgeon and District Public Healt Officer of Yamethin District and Superintendent of Yamethin District Ja (Prison). L.M. & S. (Calcutta University). A good and successful studen in the chemistry classes and always takes special interest in practica chemical work. Registered Medical Practitioner of the British Medica Council (London). Attended pulp making from bamboo for making of pape Wants to do research work in chemistry. (*Signed by*) L. B. Seal, M. Hunte

LAWRANCE, WALTER ALBERT, Lewiston, Maine, U.S.A. Professor Chemistry, Bates College. Degrees: B.A., M.A. (McMaster); M.A., Ph.I (Toronto). "Poly-nitro-compounds," *Proc. Royal Soc. Can.*, May 191 "Friedel-Crafts' Reaction," *J. Am. Chem. Soc.*, Sept. 1920. "Friede Crafts' Reaction," *J. Am. Chem. Soc.*, Dec. 1921. "Friedel-Crafts' Rea tion," *J. Am. Chem. Soc.* (in course of publication). (*Signed by*) W. Las Miller.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

*Ordinary Scientific Meeting, Thursday, April 6th, 1922, at 8 p.m.,* PROFESSOR H. E. ARMSTRONG, LL.D., F.R.S., Vice-President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of:

| | Elected. | Died. |
|---|---|---|
| Philippo Auguste Guye (Honorary Fellow) | Mar. 7th, 1912. | Mar. 27th, 1922. |
| Seward Whiting Williams | June 18th, 1891. | Aug. 25th, 1921. |

It was announced—

(1) That in order to commemorate the centenary of the birth of Pasteur the University and town of Strasbourg have decided to erect a statue facing the University where, as a professor, Pasteur commenced his career. The inauguration ceremonies, under the patronage of the President of the Republic and other distinguished men, will be held on May 1st, 1923, and will include the unveiling of the statue and the opening of an Exhibition of Hygiene and Bacteriology.

With the object of evincing the sympathy of this country with the project in view, a British Committee has been formed of the following: Chairman, Sir Charles Sherrington, G.B.E. (President of the Royal Society), Treasurer, Mr. A. Chaston Chapman, F.R.S. (President of the Institute of Chemistry), Mr. H. E. Field (President of the Institute of Brewing), Professor Percy F. Frankland, C.B.E., F.R.S., Sir John M'Fadyean, M.R.C.V.S., LL.D. (Principal of the Royal Veterinary College), Professor C. J. Martin, C.M.G., F.R.S. (Director of the Lister Institute), Sir William J. Pope, K.B.E., F.R.S., Sir James Walker, F.R.S. (President of the Chemical Society), and Sir Almroth Wright, K.B.E., F.R.S. (Principal of the Institute of Pathology and Research).

It is hoped there may be many British chemists desirous of contributing to the Memorial Fund. Contributions may be sent

to Monsieur Th. Héring, 6, Rue des Veaux, Strasbourg, or to Mr. A. Chaston Chapman, Institute of Chemistry, 30, Russell Square, W.C. 1. The subscription list will close about the end of next June.

Manufacturers and business firms in this country to whom the Exhibition may be of interest are cordially invited to offer assistance, and those able and willing to do so should communicate with Professor Borrel, 3, Rue Koeberlé, Strasbourg.

(2) That the following Committees for 1922—1923 had been appointed by the Council :

*Finance Committee.*—Messrs. E. F. Armstrong, A. Chaston Chapman, C. A. Hill, G. T. Moody, and the Officers.

*House Committee.*—Messrs. J. L. Baker, Sir Herbert Jackson, Alexander Scott, Sir William A. Tilden, E. W. Voelcker, and the Officers.

*Library Committee.*—Messrs. P. P. Bedson, O. L. Brady, Sir Thomas K. Rose, E. J. Russell, J. M. Thomson (Chairman), Sir William A. Tilden, the Editor, the Librarian, and Officers, together with the following representatives of contributing Societies: Messrs. J. L. Baker, C. Dorée, J. C. Drummond, A. Harden, C. A. Keane, R. L. Mond, and G. Senter.

*Publication Committee.*—Messrs. A. J. Allmand, O. L. Brady, C. H. Desch, I. M. Heilbron, J. T. Hewitt, J. C. Irvine, H. King, T. M. Lowry, J. W. McBain, R. H. Pickard, N. V. Sidgwick, J. F. Thorpe, and the Officers.

*Research Fund Committee.*—Messrs. H. B. Baker, D. L. Chapman, Sir James J. Dobbie, F. G. Donnan, G. G. Henderson, F. S. Kipping, R. H. Pickard, Sir William J. Pope, R. Robinson, S. Smiles, and the Officers.

The following were formally admitted Fellows of the Chemical Society : H. B. Courtney and G. Thompson.

Certificates were read for the first time in favour of :

eorge Baborovský, Ph.D., Falkensteinerova ul. 7, Brno, Czecho-Slovakia.
tanley John Bailey, B.A., The Braes, South Nutfield, Redhill.
obert Stanley Colborne, B.Sc., A.R.C.S., 57, County Road, Swindon.
ames Brierley Firth, D.Sc., F.I.C., 44, Lucknow Avenue, Mapperley Park, Nottingham.
orothea Annie Hoffert, 50, Hampstead Way, N.W. 11.
alph Henry Parker, Radio House, Wilson Road, Smethwick, Staffs.
dmond Samuels, 40, Castlereagh Street, Sydney, N.S.W.
onald William Stevenson, M.C., M.A., Eaglehurst, Ditton Hill, Surbiton.

A Certificate has been authorised by the Council for presentation o ballot under Bye-Law I (2) in favour of :

obert Swainson-Hall, Government Plantations Department, Victoria, British Cameroons, West Africa.

The following papers were read:

"Constitution of picrorocellin, a nitrogenous constituent of *Roccella fuciformis*." By M. O. FORSTER and W. B. SAVILLE.

"The determination of surface tension from the maximum pressure in bubbles." By S. SUGDEN.

"The variation of refractive index and specific gravity of benzene with temperature." By W. B. PARKER and G. THOMPSON.

"The influence of substituents on the formation and stability of heterocyclic compounds. Part I. Hydantoins." By C. K. INGOLD, S. SAKO, and J. F. THORPE.

## ORDINARY SCIENTIFIC MEETING.

The next Ordinary Scientific Meeting will be held on Thursday, May 4th, 1922, at 8 p.m., when a ballot for the election of Fellows will be held.

## INFORMAL MEETING.

The next Informal Meeting will be held on Thursday, May 18th, 1922, after the conclusion of the formal business of the Ordinary Scientific Meeting, to be held at 8 p.m.

## RESEARCH FUND COMMITTEE.

A meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W. 1., must be received on or before Thursday, June 1st, 1922.

All persons who receive grants in June, 1921, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by Thursday, June 1st.

## SETS OF THE BERICHTE AND OF THE ZENTRALBLATT.

The Society still has a few remaining sets of the *Berichte* and of the *Zentralblatt* from August, 1914, to December, 1920, inclusive, for disposal. These can be obtained, in complete sets only, from the Assistant Secretary, price £10 per set of the *Berichte*, and of the *Zentralblatt*.

The number of sets is strictly limited and application should be made without delay.

## LIST OF FELLOWS, 1922.

The Council has decided to supply the List of Fellows for 19
to those Fellows only who make application to the Assista
Secretary before August 31st, 1922.

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## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

Cornubert, R. Dictionnaire Anglais-Français-Allemand : 
mots et locutions intéressant la physique et la chimie. Paris 192
pp. xxxii + 298. 42 *fr.* (*Reference.*)
From the Publisher : M. Duno

Hale, Arthur James. Modern chemistry, pure and applie
Vol. IV. London [1922]. pp. viii + 280. ill. 16*s.* net. (*Re*
31/3/22.) From the Publishers : Messrs. Virtue & C

Imperial Institute. Indian Trade Enquiry. Reports on l
turpentine, and rosin. London 1922. pp. x + 74. 5*s.* n
(*Recd.* 1/4/22.) From the Direct

Imperial Mineral Resources Bureau. Laws and regulatio
relating to lead poisoning : being an analysis with texts of t
laws and regulations made in the chief industrial countries
prevent plumbism. By Gilbert Stone. London 1922. pp. 2
(Two copies.) 5*s.* net. From the Burea

Indian Science Congress. Handbook for the use of membe
attending the ninth meeting to be held at Madras . . . 19
Madras 1921. pp. x + 166. (*Recd.* 21/3/22.)
From Captain Clive Newcom

Lowry, Thomas Martin. Inorganic chemistry. London 19
pp. xii + 944. ill. 28*s.* net. (*Recd.* 30/3/22.)
From the Auth

Ministry of Munitions and Department of Scientific a
Industrial Research. Technical records of explosives sup
1915–1918. No. 8. Solvent recovery. London 1921. pp. iv +
ill. 3*s.* net. (*Recd.* 10/4/22.) From the Departme

Monier-Williams, Gordon Wickham. Power alcohol :
production and utilisation. London [1922]. pp. xii + 324.
21*s.* net. (*Recd.* 10/4/22.)
From the Publishers : Messrs. Henry Frowde a
Hodder & Stought

Scientific and Industrial Research, Department of. *Fuel Research Board.* A handbook on the winning and utilisation of peat. By A. Hausding. Translated from the 3rd German edition by Hugh Ryan. London 1921. pp. xxiv + 506. ill. 30*s.* net. (*Recd.* 16/3/22.) From the Department.

Sherman, Henry Clapp, and Smith, Sybil L. The vitamins. New York 1922. pp. iv + 274. ill. $4 net. (*Recd.* 21/3/22.)
From the Publishers: The Chemical Catalogue Company, Inc.

Venable, Francis P. Zirconium and its compounds. New York 1922. pp. 1–10, 15–174. $2·50 net. (*Recd.* 30/3/22.)
From the Publishers: The Chemical Catalogue Company, Inc.

## II. *By Purchase.*

Aston, Francis William. Isotopes. London 1922. pp. viii + 152. ill. 9*s.* net. (*Recd.* 14/3/22.)

Bodforss, Sven. Die Aethylenoxyde. Ihre Darstellung und Eigenschaften. (Sammlung, Vol. XXVI.) Stuttgart 1920.

Böckmann, Friedrich. Celluloid: its raw material, manufacture, properties and uses. 2nd English edition, translated from the 3rd German edition by Herbert Birtwhistle Stocks. London 1921. pp. viii + 188. ill. 8*s.* 6*d.* net. (*Recd.* 16/3/22.)

Chapman, Alfred Chaston. Einige Fortschritte auf dem Gebiete der analytischen Chemie. Translated by Oskar Baudisch. (Sammlung, Vol. XXVI.) Stuttgart 1921.

Donath, Eduard, and Lissner, A. Kohle und Erdöl. (Sammlung, Vol. XXVI.) Stuttgart 1920.

Funk, Casimir. The vitamines. Translated from the 2nd German edition by Harry E. Dubin. Baltimore 1922. pp. 502. ill. 31*s.* 6*d.* net. (*Recd.* 9/3/22.)

Grossmann, Hermann, and Wreschner, Marie. Die anomale Rotationsdispersion. (Sammlung, Vol. XXVI.) Stuttgart 1921.

Hahn, Friedrich-Vincenz von. Ueber die Herstellung und Stabilität kolloider Lösungen anorganischer Stoffe. (Mit besonderer Berücksichtigung der Sulfidsole.) (Sammlung, Vol. XXVI.) Stuttgart 1922.

Hatschek, Emil. An introduction to the physics and chemistry of colloids. 4th edition. London 1922. pp. xiv + 172. ill. 7*s.* 6*d.* net. (*Recd.* 16/3/22.)

Hurst, George H. Soaps: a practical manual on the manufacture of domestic, toilet, and other soaps. 3rd edition. By Herbert Birtwhistle Stocks. London 1922. pp. viii + 432. ill. 21*s.* net. (*Recd.* 14/3/22.)

JONES, LLEWELLYN, and SCARD, FREDERIC ISENBART. The manufacture of cane sugar. 2nd edition. London [1921]. pp xx + 482. ill. 25s. net. (*Recd.* 16/3/22.)

JULIAN, H. FORBES, and SMART, EDGAR. Cyaniding gold and silver ores. 3rd edition. By A. W. ALLEN. London 1921. pp xxiv + 418. ill. 36s. net. (*Recd.* 16/3/22.)

MEADE, ALWYNE. Modern gasworks practice. 2nd edition London 1921. pp. xii + 816. 55s. net. (*Recd.* 14/3/22.)

MELLOR, JOSEPH WILLIAM. A comprehensive treatise on inorganic and theoretical chemistry. Vols. I and II. London 1922. pp. xvi + 1066, viii + 894. ill. (*Reference.*) £6 6s. net.

NEUBURGER, MAXIMILIAN CAMILLO. Das Problem der Genesis des Actiniums. (Sammlung, Vol. XXVI.) Stuttgart 1921.

—— Neuere Ergebnisse der Forschung über die Radioaktivität des Kaliums und Rubidiums im letzten Dezennium. (Sammlung Vol. XXVI.) Stuttgart 1921.

PFEIFFER, PAUL. Organische Molekülverbindungen. (Chemie in Einzeldarstellungen, Vol. XI.) Stuttgart 1922. pp. xiv + 328 (*Recd.* 14/3/22.)

REDWOOD, SIR BOVERTON. Petroleum. 3 vols. 4th edition London 1922. pp. xxx + 1353. ill. £5 5s. net. (*Recd.* 10/3/22.)

SIMMONS, WILLIAM HERBERT, and MITCHELL, CHARLES AINSWORTH. Edible fats and oils: their composition, manufacture and analysis. 2nd edition. London 1921. pp. viii + 190. ill 10s. 6d. net. (*Recd.* 16/3/22.)

YOUNG, SYDNEY, and others. Distillation principles and processes London 1922. pp. xiv + 510. ill. 40s. net. (*Recd.* 14/3/22.)

ZEITSCHRIFT FÜR LEDER- UND GERBEREI-CHEMIE. Vol. I., etc Hamburg 1922 +. ill. (*Reference.*)

## III. *Pamphlets.*

ALEXANDER, ELIZABETH H. A bibliography of John Ferguson. (From the *Trans. Glasgow Bibliographical Soc.*, with alterations.) 1920. ill.

IMPERIAL MINERAL RESOURCES BUREAU. The Mineral Industry of the British Empire and Foreign Countries. War Period. Lead. (1913–1919.) London 1922. pp. 95.

—— —— Platinum and allied metals. (1913–1919.) London 1922. pp. 84.

—— —— Tin. (1913–1919.) London 1922. pp. 98.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. Lecture on modern applications of chemistry to crop production. By EDWARD JOHN RUSSELL. London 1922. pp. 23. ill.

MIALL, STEPHEN. The structure of the atom: notes on some recent theories. London 1922. pp. vi + 26. ill.

TADOKORO, TETSUTARO. On the spectrochemical reaction of methylfurfurol- and oxymethylfurfurol phloroglucid. (From the *J. Coll. Agric., Hokkaido Imp. Univ.*, 1921, **10**.) ill.

—— Ultraviolet spectroscopical studies on the antagonistic action of salts in organic colloidal solution. (From the *J. Coll. Agric., Hokkaido Imp. Univ.*, 1921, **10**.) ill.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 4th, 1922, at 8 p.m., Professor J. F. THORPE, C.B.E., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following Fellows:

| | Elected. | Died. |
|---|---|---|
| Sir William Phipson Beale ........................ | Dec. 5th, 1867. | April 13th. |
| Joseph Albert Hughes .............................. | Dec. 3rd, 1908. | Jan. 9th. |
| Charles Mann Luxmoore ........................... | Feb. 16th, 1893. | April 16th. |
| James Morris .......................................... | May 1st, 1919. | Mar. 31st. |

The CHAIRMAN announced:

1. That the Council had sealed the following Address of Congratulation to be presented to the Royal University of Padna on the celebration of the Seven Hundredth Anniversary of its Foundation to be held on May 14th to 17th, 1922:

THE CHEMICAL SOCIETY

TO

THE RECTOR, SENATE, PROFESSORS AND ALUMNI

OF THE

ROYAL UNIVERSITY OF PADUA.

On behalf of the Chemical Society, we have the honour to convey our warmest felicitations on the celebration of the Seven Hundredth Foundation Anniversary of the Royal University of Padua.

The knowledge that your University flourished in the 13th century, that six hundred years ago it pointed the way of learning to the peoples—not only of Italy, but of Europe—and that inscribed on the roll of its learned professors in

science are to be found the immortal names of Galileo and Morgagni, is indeed an inspiration to the whole world. It is our earnest wish that the lamp of learning, kindled so long ago in your ancient University, may continue to burn with increasing radiance.

In the name of the Fellows and Council of the Chemical Society we welcome this happy opportunity of recording our deep appreciation of the commanding position achieved by your University in the advancement of knowledge, uniting therewith our most sincere wishes for the continued prosperity of this illustrious and venerable seat of learning.

Signed on behalf of the Council of
The Chemical Society.

JAMES WALKER, President.
M. O. FORSTER, Treasurer.
(L.S.) IRVINE MASSON, JAMES C. PHILIP, } Secretaries.
ARTHUR W. CROSSLEY, Foreign Secretary.

Sealed in Council this Fourth day of May, One Thousand Nine Hundred and Twenty-Two.

2. That Mr. G. H. Gabb had presented to the Society's collection a medal of Joseph Priestley, executed by Halliday about 1804. The inscription on the reverse of the medal is taken from the tablet erected in the new Meeting House, Birmingham, to the memory of Priestley and was written by Dr. Parr.

The following were formally admitted Fellows of the Chemical Society: P. Appleyard, K. A. Burke, M. H. Cocks, K. J. Isaac, L. O. Kekwick, and H. L. Saunders.

Certificates were read for the first time in favour of:

Frank Belton, B.Sc., Athlone, Bush Hill Park, Enfield.
Robert Keith Cannan, M.Sc., 4, Antrim Mansions, N.W. 3.
Bibhu Charan Chatterjee, M.Sc., University College of Science, 92, Upper Circular Road, Calcutta, India.
Shiavaksha Hormasji, Contractor, Karanjia Building, opp. Moos Building, Grant Road, Bombay, India.
Margaret White Fishenden, D.Sc., 19, Shepherd's Hill, Highgate, N. 6.
Frederick Walter Goddard, M.A., 12, College Street, Winchester.
Edmund Langley Hirst, M.A., B.Sc., Ph.D., Ainslie Villa, Largo Road, St. Andrews.
William Job Jenkins, 37, Marston Road, Knowle, Bristol.
Peppo Joseph Levy, 42, Granville Gardens, Shepherd's Bush, W. 12.
David McCall, B.Sc., 4, Lime Street, Dundee.
Richard Edmund Anthony Mallet, B.A., Redford, Ockley, Surrey.

Ronald George Wreyford Norrish, B.A., Emmanuel College, Cambridge.
John Goodrich Oats, 3, Montpelier Terrace, Ilfracombe.
Claude Bernard Meister Platt, M.B.E., Middleton House, Beckett Road, Doncaster.
Arthur Plowman, B.Sc., A.R.C.S., A.I.C., 8, Rowantree Road, Bycullah Park, Enfield.
John Pryde, B.Sc., 4, Gowrie Street, Blackness Avenue, Dundee.
Juda Hirsch Quastel, B.Sc., A.R.C.S., A.I.C., Trinity College, Cambridge.
John Charles Smith, B.Sc., 31, Bidwell Street, Wellington, N.Z.
Valerie Emeline Sophie Swainson, B.Sc., 21, Hungerford Road, N. 7.
Nowroji Jamshedji Vazifdar, 17, Queens Road, opp. Charin Road Station, Bombay, India.
*George William Wigg*, 72nd Northumbrian Bde., R.F.A., Barrack Road, Newcastle-on-Tyne.

Messrs. C. Gilling and J. Reilly were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Brojo Kishore Banerjee, B.Sc.
Benoy Bhusan Basu, B.Sc., M.B.
Harilal Basu.
George Macdonald Bennett, M.A., M.Sc., F.I.C.
John William Blagden, M.A., Ph.D., F.I.C.
Frederick Mason Brewer.
Eric Sykes Brooks.
Fred Brumfitt.
Carlton Butler, B.Sc., A.I.C.
Charlie Lyons Carter, M.Sc., A.I.C.
Arthur Rockett Chadwick.
Leslie Ashburn Dunn.
Richard Fisher.
Francis Arthur Freeth, M.Sc., F.I.C.
*Alfred Duncan Gay.*
Douglas Creese Harrison, B.Sc.
Thomas Weatherill Harrison, B.Sc., F.I.C.
Henry Unwin Harrow.
Douglas Cecil Henry, M.A.
Herbert Hodgson.
Eusebius Holmes, B.Sc.
William Hurst.
Thomas Iredale, B.Sc.
Ethel Mary James, B.Sc.
George Lewis Kennaby, B.Sc.
Walter Albert Lawrance, M.A., Ph.D.
Edward Ingleson Lawson.
Arthur Cyric Percy Lunn, B.A.
Robert Craig McDowall.
Lingaiah Basavalingaiah Manjunath, B.A.
John Mylne Mullaly.
Harold Edward Charles Powers, B.Sc.
Akella Suryanarayana Rao, B.Sc.
Harry Lister Riley, B.Sc.
James Robinson, B.Sc.
George Allan Russell, B.Sc., A.I.C.
M. Subramania Sastry, B.A.
Ernest Arthur Seeley, B.Sc.
Brian Duncan Shaw.
Albert William Smith, B.Sc., Ph.D.
Clarence Stott, B.Sc., A.I.C.
William Thomas, B.A., M.Sc., A.I.C.
George Flaxman Underhay, B.Sc.
William Andrew Shakespeare Vardy.
John George Walters, B.Sc.
Arthur Frederick Watson, M.Sc., A.I.C.
*William Wallace Watt.*
Llywelyn Williams, B.Sc.
Harry Alexander Wood.

The following papers were read:

"On dopplerite. Studies in the composition of coal." By F. V. Tideswell and R. V. Wheeler.

"Bromo-derivatives of glyoxaline." By I. E. Balaban and F. L. Pyman.

"The properties of ammonium nitrate. Part IV. The reciprocal salt-pair $NH_4NO_3+NaCl \rightleftarrows NH_4Cl+NaNO_3$." By E. P. PERMAN.

"The reactivity of ammonia." By E. C. C. BALY and H. M. DUNCAN.

"Photocatalysis. Part II. The photosynthesis of nitrogen compounds from nitrates and carbon dioxide." By E. C. C. BALY, I. M. HEILBRON, and D. P. HUDSON.

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Ordinary Scientific Meeting, Thursday, May 18th, 1922, at 8 p.m., SIR JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of :

| | Elected. | Died. |
|---|---|---|
| Adolphus Collenette ............ | March 1st, 1883. | May 7th, 1922. |

The following were formally admitted Fellows of the Chemical Society : G. M. Bennett and J. G. Mitchell.

Certificates were read for the first time in favour of :

Harry Baines, B.Sc., 22, Henry Road, West Bridgford, Nottingham.

Victor Cecil Branson, B.Sc., A.R.C.S., A.I.C., Messrs. Naparma Oilfields, Ltd., San Fernando, Trinidad, B.W.I.

Albert Hassell, 47, Stanley Street, Tunstall, Stoke-on-Trent.

Edith Annie Peach, 43, St. Gabriel's Road, Cricklewood, N.W.2.

Clifford Dane Thomas, B.Sc., 10, Lansdowne Place, Blackheath, S.E.10.

The following Certificate has been authorised by the Council for presentation to ballot under Bye-law I (2) :

Walter Herbert Fulweiler, B.Sc., c/o The United Gas Improvement Co., Philadelphia, Pa., U.S.A.

The meeting was then adjourned and the Informal Meeting declared open. A selection of autograph letters from the Roscoe collection and of books of historical interest from the Library was exhibited.

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## LECTURE.

At the Ordinary Scientific Meeting to be held on Thursday, June 8th, 1922, at 8 p.m., in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, S.W.1, Dr. H. H. Dale, C.B.E., F.R.S., will deliver his Lecture entitled : "Chemical and Physiological Properties."

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## LIST OF FELLOWS, 1922.

*The Council has decided* to supply the List of Fellows for 1922 to those Fellows only who make application to the Assistant Secretary before August 31st, 1922.

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List of Papers received between April 7th and May 18th, 1922:

"A synthesis of *iso*brazilein and certain related anhydropyranol salts. Part II. Synthesis of *iso*hæmatein." By H. G. CRABTREE and R. ROBINSON.

"Studies in catalysis. Part XVI. The inversion of sucrose by hydrogen ion." By T. MORAN and W. C. McC. LEWIS.

"2-*p*-Dimethylaminostyrylpyridine methiodide, a new photographic sensitiser." By W. H. MILLS and W. J. POPE.

"On dopplerite. Studies in the composition of coal." By F. V. TIDESWELL and R. V. WHEELER.

"Bromo-derivatives of glyoxaline." By I. E. BALABAN and F. L. PYMAN.

"The oxidation of hexadecane and saturated fatty acids by air or oxygen." By A. H. SALWAY and P. N. WILLIAMS.

"*Estimation of lead peroxide*." By C. RAMASOMAYAJULU.

"Dyes derived from phenanthraquinone (naphthaflavindulines)." By S. C. DATTA.

"Researches on sulphuryl chloride. Part II. A new chlorinating agent; preparation of poly-chloro-derivatives of benzene." By O. SILBERRAD.

"The decomposition of benzyl disulphoxide." By J. A. SMYTHE.

"The use of iron pyrites in a Friedel-Crafts' reaction." By J. A. SMYTHE.

"The properties of ammonium nitrate. Part IV. The reciprocal salt-pair, $NH_4NO_3 + NaCl \rightleftharpoons NH_4Cl + NaNO_3$." By E. P. PERMAN.

"The reactivity of ammonia." By E. C. C. BALY and H. M. DUNCAN.

"Photocatalysis. Part II. The photosynthesis of nitrogen compounds from nitrates and carbon dioxide." By E. C. C. BALY, I. M. HEILBRON, and D. P. HUDSON.

"Attempts to prepare red sulphide dyes. Part I." By E. R. WATSON and S. DUTT.

"Limits for the propagation of flame in vapour–air mixtures. Part I. Mixtures of air and one vapour at the ordinary temperature and pressure." By A. G. WHITE.

"Studies on hypophosphorous acid. Part IV. Its reaction with cupric chloride." By A. D. MITCHELL.

"The labile nature of the halogen atom in organic compounds. Part III. The absorption spectra of bromomalonic derivatives and nitroparaffins, and their bearing on the question of an oxygen–halogen linking." By H. GRAHAM and A. K. MACBETH.

"The labile nature of the halogen atom in organic compounds. Part IV. The tautomeric hydrogen hypothesis and the removal of the halogen atom from aromatic nitro-compounds." By A. K. MACBETH.

"The action of sulphur on cuprous chloride." By F. W. PINKARD and W. WARDLAW.

"Dyes derived from phenanthraquinone. Part I. Phenanthranaphthazines." By A. C. SIRCAR and S. B. DUTT.

"Physical chemistry of the oxides of lead. Part IV. Red lead and lead sesquioxide." By S. GLASSTONE.

"The sulphilimines, a new class of organic compounds containing quadrivalent sulphur." By F. G. MANN and W. J. POPE.

"The aldehydo-salicyclic acids and their derivatives." By E. J. WAYNE and J. B. COHEN.

"The effect of an electrolyte on solutions of pure soap. Phase rule equilibria in the system sodium laurate–sodium chloride–water." By J. W. McBAIN and A. J. BURNETT.

"Investigations into the analytical chemistry of tantalum, columbium, and their mineral associates. Part III. A critical study of the volumetric estimation of columbium." By W. R. SCHOELLER and E. F. WATERHOUSE.

"Mercury compounds of hydroxybenzaldehydes." By T. A. HENRY and T. M. SHARP.

"*iso*Quinoline and the *iso*quinoline-reds." By J. E. G. HARRIS and W. J. POPE.

"Studies in optically active dyes. Part I. Camphoreins." By B. K. SINGH, R. RAI, and R. LAL.

"The hydroferrocyanides and hydroferricyanides of the organic bases." Part I. By W. M. CUMMING.

"The viscosity of cellulose in cuprammonium hydroxide solution. Part I. The determination of the viscosity." By R. A. JOYNER.

"The oxidising and reducing properties of sulphur dioxide. Part IV. Mercury chlorides." By L. M. STEWART and W. WARDLAW.

"The conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part IV. Products formed from halogen derivatives of muconic acid. The constitution of muconic acid." By J. P. C. CHANDRASENA and C. K. INGOLD.

"Studies in the coumaranone series. Part II. The preparation of 6- and 4-chlorocoumaran-2-ones and their conversion into 4- and 2-chloroflavanols respectively and some derivatives of o- and *p*-chlorophenoxyacetic acids." By T. H. Minton and H. Stephen.

"The preparation of *o*-, *m*-, and *p*-nitrophenoxyacetic acids and various nitrotolyloxyacetic acids and their derivatives." By T. H. Minton and H. Stephen.

"Some properties of hydrogen desorbed from platinum and palladium." By P. Anderson.

"The reactivity of doubly-conjugated unsaturated ketones. Part III. Unsymmetrical hydroxy- and methoxy-derivatives." By J. S. Buck and I. M. Heilbron.

"Phenopyryllium salts of distyryl ketones. Part I." By J. S. Buck and I. M. Heilbron.

"The mathematics of the dicyclic colour theory and a new theory of the nitrogen atom." By J. Moir.

"Physical chemistry of the oxides of lead. Part V. The electromotive behaviour of lead dioxide." By S. Glasstone.

"Studies of the constitution of soap solutions. Sodium behenate and sodium nonylate." M. Taylor.

"Studies in the anthracene series. Part II." By E. de B. Barnett and J. W. Cook.

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## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

Actualités de Chimie Contemporaine. Publiées sous la direction de A. Haller. 1st series. Paris 1922. pp. viii + 326. ill. 12 *fr.* (*Recd.* 11/4/22.)

From the Publisher: M. Gaston Doin.

Imperial Mineral Resources Bureau. The Mineral Industry of the British Empire and Foreign Countries. War Period. Copper (1913—1919). London 1922. pp. 204. 4*s.* net. (*Recd.* 1/5/22.)

—— —— Gold (1913—1919). London 1922. pp. 366. 6*s.* net. (*Recd.* 11/4/22.) From the Bureau.

Purvis, John Edward, and Hodgson, Thomas Reginald. The chemical examination of water, sewage, foods and other substances. 2nd edition. Cambridge 1922. pp. viii + 346. 20*s.* net. (*Recd.* 3/5/22.) From the Syndics, Cambridge University Press.

Staley, Ralph. Town gas manufacture: a practical introductory treatment of the equipment and processes of an average gas works. London 1922. pp. xii + 108. ill. 2*s.* 6*d.* net. (*Recd.* 1/5/22.) From the Publishers: Sir Isaac Pitman & Sons.

II. *By Purchase.*

SAINTE-CLAIRE DEVILLE, ÉMILE. Manuel de chimie gazière: méthodes et procédés des essais et analyses en usage à l'usine expérimentale de la villette de la Société du Gaz de Paris. Paris 1921. pp. viii + 208. ill. (*Recd.* 2/5/22.)

TRIVELLI, ADRIAAN PETER HERMAN, and SHEPPARD, SAMUEL EDWARD. The silver bromide grain of photographic emulsions. Rochester, N.Y. 1921. pp. 144. ill. 16*s*. net. (*Recd.* 1/5/22.)

VRIES, OTTO DE. Estate rubber: its preparation, properties and testing. Batavia 1920. pp. xii + 650. ill. 40*s*. net. (*Recd.* 2/5/22.)

WILLGERODT, CONRAD. Die organischen Verbindungen mit mehrwertigem Jod. (Chemie in Einzeldarstellungen, Vol. VII.) Stuttgart 1914. pp. xii + 266. (*Recd.* 2/5/22.)

ZEITSCHRIFT FÜR LEDER- UND GERBEREI-CHEMIE. Vol. I, etc. Hamburg 1921 +. ill. (*Reference.*)

ZEITSCHRIFT FÜR PFLANZENERNÄHRUNG UND DÜNGUNG. A. Wissenschaftlicher Teil. B. Wirtschaftlich-Praktischer Teil. Vol. I, etc. Leipzig 1922 +. (*Reference.*)

## CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, JUNE 15TH, 1922.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

BADOROVSKÝ, GEORGE, Ph.D. (Prague), Brno, Falkensteinerova, ul. 7. Professor in the Technical High School of Brno, Tchechoslowackia. Member of the Société chimique de France, Tchechoslowack Chemical Society, formerly member of the American Electrochemical Society, formerly Professor in the University of Prague. 1900–1905 assistant, 1905–1911 lecturer in physical chemistry; 1911–1912 professor of physical chemistry in the Czech University of Prague; since 1912 professor of physical chemistry in the Czech Technical High School of Brno. Publications on different physico-chemical and electrochemical subjects in following periodicals: *Bulletin of the Czech Acad. of Science, Zeit. f. phys. Chem., Zeit. f. Elektrochem., Phys. Zeitschr., Chem. Listy.* Books: "Electrochemistry" (with Prof. F. Plzák), "Theoretical and Physical Chemistry" (1920) (boh.). (*Signed by*) Gerald Druce, A. Šimek, J. Heyrovský.

BAILEY, STANLEY JOHN, The Braes, South Nutfield, Surrey. Student (Cambridge University), Natural Science Tripos, Part I, in 1921, including Chemistry. (*Signed by*) T. Martin Lowry, Alfred Greeves, Hamilton McCombie, William J. Pope.

Baines, Harry, 22, Henry Rd., West Bridgford, Notts. British. Research Student. B.Sc. (Lond.), external, 1st Class Hons. in Chemistry. Now engaged on research course. (*Signed by*) F. Stanley Kipping, S. J. Pentecost, F. C. Laxton.

Belton, Frank, "Athlone," Bush Hill Park, Enfield. Headmaster, County Secondary School, Edmonton, N.9. (1) B.Sc. (London), Chemistry at Final Exam. (2) Studied chemistry at the Royal Technical College, Salford; with a short course at the Royal College of Science, London. (3) Head of Science Dept. and teacher of chemistry, Central Higher Grade School, Salford. (4) Author of text-books on physics and chemistry. (*Signed by*) B. Prentice, E. Clark, E. Green.

Branson, Victor Cecil, Naparma Oilfields, Ltd., San Fernando, Trinidad, B.W.I. Analytical Chemist. A.R.C.Sc. (1st class chemistry), B.Sc. Lond. (1st class honours in Chemistry), A.I.C. Chemist to the Naparma Oilfields, Ltd., since Jan. 1920. (*Signed by*) L. H. Parker, James C. Philip, H. B. Baker.

Cannan, Robert Keith, 4, Antrim Mansions, N.W.3. Assistant in Biochemistry, University College, London. Several papers in *Biochemical Journal* and *Journal of Physiology*. M.Sc. (Lond.) in Biochemistry. (*Signed by*) J. C. Drummond, R. H. A. Plimmer, Irvine Masson.

Chatterjee, Bibhu Charan, Ariadah, 24, Perganas, Bengal. Research Scholar in Chemistry. B.Sc. (Hons. in Chemistry), 1919; M.Sc. in Chemistry, 1921; first in Class 1; conducted a piece of research work in organic chem. entitled, "On carbamic esters; chlorine as a simultaneous oxidising and chlorinating agent"; Sir T. N. Palit Research Scholar in Chemistry, Calcutta University. (*Signed by*) P. C. Rây, R. L. Datta, J. N. Mukherjee.

Colborne, Robert Stanley, 57, County Road, Swindon. Research Student in Physical Chemistry (Imperial College, London). Student at Imperial College since 1919 (Oct.); A.R.C.S. (1st Class) 1921 (July); B.Sc. (Hons. 1st Class) 1921 (Nov.). (*Signed by*) H. B. Baker, M. A. Whiteley, James C. Philip, H. J. T. Ellingham.

Contractor, Shiavaksha Hormasji, F.N.B.A., F.S.Sc. (Lond.), Karanjia Building, opp. Moos Building, Grant Rd., Bombay. Scientist, Artist and Craftsman. Inventor of gold mirror glasses; Permanent blotters; Sizing Composition, etc. Recipient of 50 gold, silver, and bronze medals, and hundreds of diplomas at the world's various exhibitions. (*Signed by*) J. C. Mascarenhas, N. M. Bhathena, D. D. Kanga.

Firth, James Brierley, 44, Lucknow Avenue, Mapperley Park, Nottingham. Lecturer in Chemistry, University College, Nottingham. D.Sc. (Manc.), M.Sc. (Dunelm), F.I.C. Author or joint-author of some sixteen published researches, most of which have appeared in the *Journal of the Chemical Society*. (*Signed by*) F. S. Kipping, Henry Stephen, J. E. Myers, Colin Campbell, Norman Smith, Arnold Weston.

Fishenden, Margaret White, 19, Shepherds Hill, Highgate, N.6. Scientific Investigator for Fuel Research Board. 1909, B.Sc. (Manchester), 1st Class Honours Physics; 1919, D.Sc. Have published a number of papers on Meteorology (upper air) and conditions in weaving factories and spinning mills. Also the following: "The Coal Fire" (Special Report, No. 3, of Fuel Research Board). "The Efficiency of Low Temperature Coke in Domestic Appliances" (Technical Paper, No. 3, of Fuel Research Board). (*Signed by*) George Beilby, Harold B. Dixon, Frank Lee Pyman.

Goddard, Frederick Walter, 12, College St., Winchester. Assistant Master, Winchester College. M.A. (Cantab.); 1st Class Nat. Science Tripos

(1st Class Chemistry, Physics, Mineralogy); 1st Class Maths. Tripos, Pt. 1. War Service. Five years teaching Chemistry at Win. Coll. to Scholarship Candidates and post scholarship. Head of Chem. Dept., Win. Coll. (*Signed by*) Llewellyn L. Garbutt, D. Ll. Hammick, A. J. Berry.

HASSELL, ALBERT, 47, Stanley Street, Tunstall, Stoke-on-Trent. Science Master, Denstone College, Staffs. Chemistry Master, Denstone College, Staffs. I wish to obtain the Transactions so as to keep in touch with current chem. literature. (*Signed by*) Joseph West, H. V. Thompson, F. H. Clews.

HIRST, EDMUND LANGLEY, Ainslie Villa, Largo Rd., St. Andrews. Assistant in Chemistry Department, University of St. Andrews. Degrees: M.A., B.Sc., Ph.D. Assistant in Chemistry at St. Andrews University from October 1920. Publication: "The constitution of the disaccharides, Part V (Cellobiose)," by Walter Norman Haworth and Edmund Langley Hirst (T., 1921, **119**, 193). (*Signed by*) J. C. Irvine, R. Robinson, R. C. Menzies, A. Killen Macbeth.

HOFFERT, DOROTHEA ANNIE, 50, Hampstead Way, London, N.W.11. Research worker under the Food Investigation Board. 1916–1920, four years' experience in analytical and research work on dopes and varnishes for aeroplanes (war work). One year, 1920–1921, student in training for research, Cambridge University, with grant from Scientific and Industrial Research Department. (*Signed by*) William J. Pope, W. H. Mills, Charles T. Heycock, Frances M. Hamer, Ida Smedley Maclean, J. N. Goldsmith.

JENKINS, WILLIAM JOB, 37, Marston Road, Knowle, Bristol. Research Chemist. Plant chemist at H.M. Factory, Pembrey, 1915–1918. Research Chemist at Messrs. Nobels Ardeer Factory, 1920–1921. Research worker under Department of Scientific and Industrial Research, 1921–1922. (*Signed by*) Wm. Rintoul, N. Picton, R. A. Joyner, Wm. Barbour.

LEVY, PEPPO JOSEPH, 42, Granville Gardens, Shepherds Bush, London W.12. Spanish. Chemist (M.F.G.) intending. I am a student at the day school of Chemistry of the Polytechnic and wish to follow the latest developments in chemical science, and to use the Society's library. (*Signed by*) Frank E. Weston, W. H. Collier, Frank Matthews.

MCCALL, DAVID, 4, Lime Street, Dundee. Head of Pharmacy Dept., Technical College, Dundee. Degree of B.Sc. (St. Andrews), July 1919. Diploma of Pharmaceutical Chemist, April 1922. Member of Pharmaceutical Society of Gt. Britain. Lecturer on Botany, Pharmacy, and Materia Medica. Head of Pharmacy Dept., Technical College, Dundee, 1919. (*Signed by*) Alex. McKenzie, John S. Lumsden, John S. W. Boyle, John Foggie, H. J. Plenderleith.

MALLET, RICHARD EDMUND ANTONY, "Redford," Ockley, Surrey. Research Chemist. B.A. of Oxford University. Honours degree passed with distinction. Now employed as chemist at the British Museum. Have been engaged in research work at Oxford with Prof. T. R. Merton, F.R.S. (*Signed by*) Alexander Scott, D. Ll. Hammick, C. N. Hinshelwood, H. R. Raikes, H. Hartley.

NORRISH, RONALD GEORGE WREYFORD, Emmanuel College, Cambridge, and 48, Kimberley Rd., Cambridge. Research Student in Photochemistry. Scholar of Emmanuel College, Cambridge. Natural Sciences Tripos, Part I, Class I. Natural Sciences Tripos, Part II Chemistry), Class I. Paper: "The Transition Elements and the Octet Theory," *Chem. News*, 1922, **124**, 16–22. My reason for seeking admission is that I hope to make the study of Chemistry my chief occupation and interest in life. (*Signed by*) W. J. Pope, W. H. Mills, Eric K. Rideal, T. M. Lowry.

Oats, John Goodrich (junr.), 3, Montpelier Terrace, Ilfracombe. Engineering Student at R. A. Lister & Co., Dursley. Also chemical student (private laboratory). Student of metallurgy, chemistry, and analysis; holding a diploma from the International Correspondence Schools, including the subjects: *mathematics, physics*, inorganic chemistry, qualit. analysis, quant. analysis, and the manufacture of iron and steel. (*Signed by*) F. Southerden, Alfred L. Grey, R. Barton, G. F. Hall, Ernest F. Hooper, Jas. Walker.

Parker, Ralph Henry, "Radio House," Wilson Rd., Smethwick, Staffs. Student in Electrical and Mechanical Engineering and allied subjects. Research Student. (1) Took the 3 years' course in physics (mechanics, heat, electricity, and magnetism) at the (full time) Junior Day Technical School, Smethwick, years 1915–1918. (2) For three years continued with part day classes, 2 years' evening tuition, also matriculation class in chemistry, Smethwick Municipal Tech. (3) Studying Organic Chemistry at present time (1922). I will endeavour to forward the interests of the Society to the best of my ability and endeavour to keep abreast with modern chemical science. (*Signed by*) Arthur Adams, Joseph Lones, J. H. Wood.

Peach, Edith Annie, 43, St. Gabriel's Road, Cricklewood, N.W.2. Student of Chemistry at University College, London. Desirous of receiving the *Journal* and of using the Library. (*Signed by*) Irvine Masson, F. G. Donnan, J. C. Drummond.

Platt, Claude Bernard Meister, *Captain*, M.B.E., R.E., *Middleton* House, Beckett Rd., Doncaster. Colliery Chemist, and Fuel Technologist. Two years as assistant to Prof. R. V. Wheeler, D.Sc., F.I.C., F.C.S.; engaged on research on spontaneous combustion of coal, composition of coal, research on explosions in mines and general laboratory work at Home Office Experimental Station. 2nd year Imperial College of Science and Technology (interrupted by the war). During war engaged on Army Wireless Telegraphy. At present chemist to Doncaster Collieries Association, Ltd., and assistant to Hot and Deep Mines Research Committee of Dept. of Scientific and Industrial Research. Published in *Trans. Chem. Soc.*, 1913, **103**, 1713. M.Soc.C.I., A.M.I.Min.E. Twelve months' experience on technical side of boiler practice—especially as regards fuel combustion. (*Signed by*) R. Lessing, W. Payman, R. V. Wheeler.

Plowman, Arthur, 8, Rowantree Rd., Bycullah Park, Enfield. Research Student. B.Sc. (Lond.), A.R.C.S., A.I.C. (*Signed by*) R. Winton West, G. A. R. Kon, E. H. Farmer.

Pryde, John, 4, Gowrie St., Blackness Ave., Dundee. Research Chemist, St. Andrews University, N.B. Degree: B.Sc. (Pure Science). 1851 *Exhibition* Research Scholar, 1921. Publication (with J. A. Hewitt): "Metabolism of Carbohydrates, Pt. 1," *Biochem. J.*, XIV, 3 and 4, 395. (*Signed by*) J. C. Irvine, R. Robinson, R. C. Menzies, A. Killen Macbeth.

Quastel, Juda Hirsch, Trinity College, Cambridge. Research Student, Biochemical Dept., Cambridge. Obtained A.R.C.S. (Lond. First Cl.), June 1921; elected Associate of Institute of Chemistry, June 1921; obtained B.Sc. Hons. (Lond. First Cl.) in October 1921. Accepted as candidate for Ph.D. (Cambridge). I wish to receive the Society's publications and to take part in its activities. (*Signed by*) F. G. Hopkins, H. B. Baker, James C. Philip.

Samuels, Edmond, 40, Castlereagh St., Sydney, N.S.W. Pharmaceutical Chemist. Chemistry course, Sydney University. Interested in preparation of pharmaceutical products for physicians' use. Originator of several

medicinal products. Member of Pharmaceutical Society of N.S.W.; member of Millions Club, N.S.W.; member of Justices Association, N.S.W. (*Signed by*) J. Laker Macmillan, G. Spurge, Francis L. Watt.

SMITH, JOHN CHARLES, 31, Bidwell Street, Wellington, N.Z. Student of Chemistry. B.Sc. (N.Z.) 1919–20. Thesis on "The Condensation of Phenolic Substances with Basic Imino-haloids," presented for the degree of M.Sc. (N.Z.), Nov. 1921. (*Signed by*) F. P. Worley, W. F. Short, A. H. Bowell.

STEVENSON, RONALD WILLIAM, M.C., M.A., *Major*, Eaglehurst, Ditton Hill, Surbiton, Surrey. Manufacturing Chemist, Analytical and Research work. Director, Messrs. Stevenson and Howell, Ltd., Manufacturing Chemists. M.A., Cambridge (Science). (*Signed by*) Arthur Hutchinson, William Stevenson, Vernon J. Tilley.

SWAINSON, VALERIE EMELINE SOPHIE, 21, Hungerford Rd., N.7. Secondary School teacher (teaching Chemistry up to Intermediate Standard). B.Sc. (Hons.) Lond. in Chemistry. Demonstrator (temporary), mainly in Inorganic Chemistry, for two terms, at University College, Dundee (Jan.–June, 1921). (*Signed by*) H. Crompton, M. S. Crewdson, J. F. Spencer.

THOMAS, CLIFFORD DANE, 10, Lansdowne Place, Blackheath, S.E.10. British. Research Chemist. Second Class Honours, B.Sc., 1920. One year's research under Dr. O. L. Brady at University College. 1920–1921. Junior Research Assistant at Research Dept., Woolwich. (*Signed by*) Eustace E. Turner, Sydney A. Pearman, W. J. Powell.

VAZIFDAR, NOWROJI JAMSHEDJI, 17, Queens Road, Opp. Charin Road Station, Bombay. First Assistant Chemical Analyser to Government. L.M. & S. Bombay. Teacher in Chemistry, Grant Medical College, Bombay. Chemical analyser to Govt. for Sind, Karachi, 1914–15; 1916–17. Author of "Physiology of the Nervous System and Special Senses." Coach in physiology for the last 15 years. (*Signed by*) D. D. Kanga, M. J. Gajjar, K. G. Naik.

WIGG, GEORGE WILLIAM, 72nd Northumbrian Bde., R.F.A., Barrack Rd., Newcastle-on-Tyne. *Lt., R.F.A. 4th–5th year medical student, University* of Durham, College of Medicine. 3rd year honours chemistry student, Armstrong college, Newcastle-on-Tyne. (*Signed by*) W. N. Haworth, Frank M. Irvine, D. Arthur Ruell.

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The following Certificates have been authorised by the Council for presentation to ballot under Bye-law I (2):

HALL, ROBERT SWAINSON, F.L.S., F.A.M.S., c/o *Govt. Plantations Dept.*, Victoria, British Cameroons, West Africa. Supt. of agriculture to Nigerian Government. Three years' training in chemistry, Waterloo Secondary School, Oldham, Lancs. Four years' practical experience in agricultural chemistry in Portuguese Congo, S.W. Africa. Contribution to science mostly in mycological and agricultural matter; see *Kew Bulletin, Bull. of Imperial Institute*, etc. (*Signed by*) John Taylor.

FULWEILER, WALTER HERBERT, Wallingford, Pa., U.S.A. Chemical Engineer with The United Gas Improvement Co., Phila., Pa. B.S. in Chemistry, University of Pennsylvania, 1901. Chemist with Phila. Gas Works, 1901–1902. Chief chemist, The United Gas Improvement Co., 1913–1920. Chemical engineer, The United Gas Improvement Co., 1920–date. (*Signed by*) H. Jermain Creighton.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 1st, 1922, at 8 p.m., Professor T. M. Lowry, C.B.E., F.R.S., Vice-President, in the Chair.

The Chairman *referred to the loss sustained by the Society*, through death, of :

| | Elected. | Died. |
|---|---|---|
| George Robertson Hislop .................. | Jan. 20th, 1870. | May 18th, 1922. |

The following were formally admitted Fellows of the Chemical Society : A. D. Gay and E. A. Seeley.

Certificates were read for the first time in favour of :

Allin Cottrell, 3, Oxford Terrace, Edinburgh.
Reginald William Griffiths, B.Sc., 137, Holly Road, Handsworth, Birmingham.
John Watson Jenkin, B.Sc., A.I.C., Tregardock, St. Austell.
Ghulam Safdar Khan, B.Sc., Veterinary College, Lahore, India.
Hiroshi Nomura, Chemical Institute, Imperial University, Sendai, Japan.
Harold Pickles, The Gasworks, Kildwick, Keighley.
Stephen John Watson, B.Sc., 35, Oakfield Terrace, Gosforth, Newcastle-on-Tyne.
Alexander Mitchell Williams, M.A., D.Sc., Shirley Institute, Didsbury, Manchester.

The following papers were read :

"The reactivity of doubly-conjugated unsaturated ketones. Part III. Unsymmetrical hydroxy- and methoxy-derivatives." By J. S. Buck and I. M. Heilbron.

"Phenopyryllium salts of distyryl ketones. Part I." By J. S. Buck and I. M. Heilbron.

"*Ring-chain tautomerism.* Part II. The effect of the gem-diethyl group on the carbon tetrahedral angle." By S. S. Deshapande and J. F. Thorpe.

Ordinary Scientific Meeting, held in the Lecture Hall of the Institution of Mechanical Engineers, on Thursday, June 8th, 1922, at 8 p.m., Professor H. E. ARMSTRONG, LL.D., F.R.S., Vice-President, in the Chair.

Dr. H. H. Dale, C.B.E., F.R.S., delivered his Lecture entitled: "Chemical and Physiological Properties." A vote of thanks to the Lecturer, proposed from the Chair, and seconded by Mr. Francis H. Carr, was carried with acclamation, and acknowledged by Dr. Dale.

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Ordinary Scientific Meeting, Thursday, June 15th, 1922, at 8 p.m., Sir JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of:

| | Elected. | Died. |
|---|---|---|
| William Gowland | Feb. 2nd, 1871. | June 10th. |
| Thomas Henry Johnson | May 5th, 1921. | Feb. 19th. |

The following were formally admitted Fellows of the Chemical Society: R. A. Fitzsimons, H. U. Harrow, E. M. James, and H. L. Riley.

Certificates were read for the first time in favour of:

William Leslie Carter, Ellesmere, Bloxcidge Street, Langley Green, Birmingham.

Wilfred Thomas Grey Davies, B.Sc., Plas y Coed, Derllwyn Road, Tondu, Bridgend.

*Roy Gardner, B.Sc., Technical High School, Dunedin, New Zealand.*

John Ernest Jewell, 34, Grove End Road, St. John's Wood, N.W. 8.

Charles William Moorhead, 23, Newbridge Road, Bath.

Albert Bramah Pearce Page, A.R.C.S., 27, Tanza Road, Hampstead, N.W. 3.

Arthur Scholefield, Poulton Hey, Bromborough, Birkenhead.

Stanley James Corrall Snedker, The Rowans, Wood Hey, Rock Ferry, Birkenhead.

Dr. H. M. Atkinson and Dr. P. C. Austin were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

George Baborovský, Ph.D.
Stanley John Bailey, B.A.
Harry Baines, B.Sc.
Frank Belton, B.Sc.
Victor Cecil Branson, B.Sc., A.R.C.S., A.I.C.
Robert Keith Cannan, M.Sc.
Bibhu Charan Chatterjee, M.Sc.
Robert Stanley Colborne, B.Sc., A.R.C.S.
James Brierley Firth, D.Sc., F.I.C.
Margaret White Fishenden, D.Sc.
Walter Herbert Fulweiler, B.S.
Frederick Walter Goddard, M.A.
Robert Swainson Hall.
Albert Hassell.

Edmund Langley Hirst, M.A., B.Sc., Ph.D.
Dorothea Annie Hoffert.
William Job Jenkins.
Peppo Joseph Levy.
David McCall, B.Sc.
Richard Edmund Antony Mallet, B.A.
Ronald George Wreyford Norrish, B.A.
*John Goodrich Oats (Junr.).*
Ralph Henry Parker.
Edith Annie Peach.
Claude Bernard Meistor Platt, M.B.E.
Arthur Plowman, B.Sc., A.R.C.S., A.I.C.
John Pryde, B.Sc.
Juda Hirsch Quastel, B.Sc., A.R.C.S.
Edmond Samuels.
John Charles Smith, B.Sc.
Ronald William Stevenson, M.C., M.A.
Valerie Emeline Sophie Swainson, B.Sc.
Clifford Dane Thomas, B.Sc.
Nowroji Jamshedji Vazifdar.
George William Wigg.

The following papers were read:

"Ring-chain tautomerism. Part III. The occurrence of tautomerism of the three-carbon (glutaconic) type between a homocyclic compound and its unsaturated open-chain isomeride." By C. K. INGOLD, E. A. PERREN, and J. F. THORPE.

"The tautomerism of dyads. Part I. Experiments on the detection of tautomeric equilibria in hydrocyanic acid." By E. H. USHERWOOD.

## LIST OF FELLOWS, 1922.

The List of Fellows for 1922 is being prepared, and changes of address received after July 31st, 1922, cannot be included therein. Fellows whose Christian names and degrees do not appear in full are particularly requested to notify the Assistant Secretary.

*Owing to the heavy cost of printing, the List will be sent only* to those Fellows who make application prior to August 31st, 1922.

## THE LIBRARY.

The Library will be closed for Stocktaking from Monday, August 7th, until Saturday, August 19th, 1922, inclusive.

During the four weeks August 21st to September 16th the Library will close daily at 5 p.m.

List of Papers received between May 19th and June 15th, 1922:

"The interaction of sodium chloride and silica." By F. H. CLEWS and H. V. THOMPSON.

"Ring-chain tautomerism. Part II. The effect of the gem-diethyl group on the carbon tetrahedral angle." By S. S. DESHAPANDE and J. F. THORPE.

"Dyes derived from saccharine. The sulphim-phthaleins." By S. DATTA.

"Dyes derived from diphenyl-ketipic-dinitrile." By S. DATTA and N. K. SEN.

"Thermal expansion of gelatin gels." By A. TAFFEL.

"The rôle of protective colloids in catalysis. Part II." By T. IREDALE.

"The chlorinated dialkyl sulphides." By W. J. POPE and J. L. B SMITH.

"Gallotannin. Part XIII. The identity of digallic acid from gallotannin with synthetic *m*-digallic acid." By M. NIERENSTEIN and C. W. SPIERS.

"Experiments on the synthesis of the polyacetic acids of methane. Part VI. Conditions of formation by the cyanoacetic ester method of unstable methanetriacetic esters and a new synthesis of methanetriacetic acid." By C. K. INGOLD and E. A. PERREN.

"Tables of average specific and atomic heat capacities of chemical elements in the order of the increment of the atomic weight and their interpretations. The law of Dulong and Petit." By P. N. TCHIRVINSKY.

"The dissociation pressures of hydrated double sulphates. Part I. Hydrated cupric alkali sulphates." By R. M. CAVEN and J. FERGUSON.

"The action of sodium sulphite on lead iodide." By G. SINGH.

"2 : 3 : 6-Trimethyl glucose." By J. C. IRVINE and E. S STEELE.

"Researches on the constitution of coal." By S. R. ILLINGWORTH.

"The composition of paraffin wax. Part II." By F. FRANCIS, C. M. WATKINS, and R. W. WALLINGTON.

"Ring-chain tautomerism. Part III. The occurrence of tautomerism of the three-carbon (glutaconic) type between a homocyclic compound and its unsaturated isomeride." By C. K INGOLD, E. A. PERREN, and J. F. THORPE.

"Note on the effect of a magnetic field on catalysis by ions in the presence of a para-magnetic salt." By W. E. GARNER and D. N JACKMAN.

"Reciprocal induced polarity effects in cresols and their derivatives. Properties of the isomeric methoxybenzyl bromides." By A LAPWORTH and J. B. SHOESMITH.

"Intermetallic actions. The system aluminium–arsenic." By Q. A. MANSURI.

"The tautomerism of dyads. Part I. Experiments in the detection of tautomeric equilibria in hydrocyanic acid." By E. H USHERWOOD.

"The nitro-derivatives of metanitrodimethylaniline." By A. FORSTER and W. COULSON.

"Catalytic racemisation of optically active acid amides." By A. MCKENZIE and I. A. SMITH.

"The sorption of phosgene by beech wood charcoal." By H. M. BUNBURY.

"The adsorption of uranium-*X* and its *isotope thorium by basic* ferric acetate." By A. C. BROWN.

"The reactions of cellulose with sodium chloride and other neutral salt solutions. Part I. Preliminary survey." By H. MASTERS.

"The imino-aryl ethers. Part I. *N*-Phenylbenzimino-*m*-hydroxyphenyl ether and the synthesis of 2 : 4-dihydroxybenzophenone." By A. W. CHAPMAN.

"The intermolecular condensation of methylethyl ketone in the presence of carbide." By O. BECKER and J. F. THORPE.

"The equilibrium in systems composed of water and alcohols. The system methyl alcohol–water." By N. A. PUSHIN and A. A. GLAGOLEVA.

"The equilibrium in the system dinitrobenzene–urethane." By N. A. PUSHIN and A. FIOLETOVA.

"The chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part III. Intra-annular tautomerism of α-campholytic acid." By J. P. C. CHANDRASENA, C. K. INGOLD, and J. F. THORPE.

"Adsorption and catalysis in Fuller's earth." By E. K. RIDEAL and W. THOMAS.

"The formation and stability of *spiro*-compounds. Part VIII. The Dieckmann-Komppa reaction." By F. DICKENS, G. A. R. KON, and J. F. THORPE.

"The cyanine dyes. Part V. The virtual tautomerism of the *thio-cyanines*." By W. H. MILLS and W. T. K. BRAUNHOLTZ.

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## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

BERNTHSEN, AUGUST. A textbook of organic chemistry. New edition, revised to date. By JOHN JOSEPH SUDBOROUGH. London 1922. pp. xvi + 908. 12*s*. 6*d*. net. (*Recd.* 16/5/22.)

From the Publishers : Messrs. Blackie & Son.

BROOKS, BENJAMIN TALBOTT. The chemistry of the non-benzenoid hydrocarbons and their simple derivatives. New York 1922. pp. 612. ill. $7 net. (*Recd.* 11/5/22.)

From the Publishers : The Chemical Catalog Company, Inc.

DUCLAUX, JACQUES. Les colloïdes. 2nd edition. Paris 1922. pp. x + 306. 10 *fr.* (*Recd.* 13/6/22.)

From the Publishers : MM. Gauthier-Villars et Cie.

FALK, KAUFMAN GEORGE. Catalytic action. New York 1922. pp. 172. $2·50 net. (*Recd.* 8/6/22.)

From the Publishers : The Chemical Catalog Company, Inc.

FRIEND, JOHN NEWTON. The chemistry of combustion. London 1922. pp. viii + 110. ill. 4*s.* net. (*Recd.* 15/5/22.)

From the Publishers : Messrs. Gurney & Jackson.

HICKS, WILLIAM MITCHINSON. A treatise on the analysis of spectra : based on an essay to which the Adams prize was awarded in 1921. Cambridge 1922. pp. viii + 326. ill. 35*s.* net. (*Recd.* 11/5/22.) From the Syndics, Cambridge University Press.

IMPERIAL MINERAL RESOURCES BUREAU. Iron ore. (Summary of information as to the present and prospective iron-ore supplies of the world.) Part I. United Kingdom. London 1922. pp. 238. ill. 6*s.* net. (*Recd.* 7/6/22.)

—— The Mineral Industry of the British Empire and Foreign Countries. War Period. Coal, coke, and by-products (1913—1919). Part II. London 1922. pp. 160. ill. 6*s.* 6*d.* net. (*Recd.* 29/5/22.) From the Bureau.

KEMPTON, PERCIVAL HENRY SYDNEY. Industrial nitrogen : the principles and methods of nitrogen fixation and the industrial applications of nitrogen products in the manufacture of explosives, fertilizers, dyes, etc. London 1922. pp. xii + 104. ill. 2*s.* 6*d.* net. (*Recd.* 2/6/22.)

From the Publishers : Sir Isaac Pitman & Sons.

KNOX, JOSEPH. The fixation of atmospheric nitrogen. 2nd edition. London 1921. pp. viii + 124. ill. 4*s.* net. (*Recd.* 15/5/22.) From the Publishers : Messrs. Gurney & Jackson.

LAURIE, ARTHUR PILLANS. Building materials : an introduction to the study of the principal materials used in building construction. Edinburgh 1922. pp. viii + 188. ill. 6*s.* net. (*Recd.* 15/5/22.)

From the Publishers : Messrs. Oliver & Boyd.

PLIMMER, VIOLET G., and PLIMMER, ROBERT HENRY ADERS. Vitamins and the choice of food. London 1922. pp. xii + 164. ill. 7*s.* 6*d.* net. (*Recd.* 22/5/22.)

From the Publishers : Messrs. Longmans, Green & Co.

SHREVE, RANDOLPH NORRIS, WATSON, WARREN N., and WILLIS, A. R. Dyes classified by intermediates. Dyes tabularly arranged under each intermediate, with statistical and other data for both dyes and intermediates. Glossary of dye and intermediate names alphabetically arranged. New York 1922. pp. ii + 632. $10 net. (*Recd.* 31/5/22.)

From the Publishers : The Chemical Catalog Company, Inc.

STEWART, ALFRED WALTER. Some physico-chemical themes. London 1922. pp. xii + 420. ill. (*Reference.*) 21*s*. net.
From the Publishers : Messrs. Longmans, Green & Co.

II. *By Purchase.*

BUDOWSKI, I. Die Naphthensäuren. Berlin 1922. pp. vi + 116. ill. (*Recd.* 31/5/22.)

FODOR, ANDOR. Das Fermentproblem. Dresden 1922. pp. x + 280. ill. (*Recd.* 23/5/22.)

FUCHS, WALTER. Der gegenwärtige Stand des Gärungsproblems. (Sammlung, Vol. XXVII.) Stuttgart 1922. (*Reference.*)

GLAZEBROOK, SIR RICHARD. [Editor.] A dictionary of applied physics. Vol. I., etc. London 1922 +. ill. (*Reference.*)

GUILLET, LÉON, and PORTEVIN, ALBERT. An introduction to the study of metallography and macrography. Translated by LEONARD TARVENER. London 1922. pp. xvi + 290. ill. 30*s*. net. (*Recd.* 13/6/22.)

KEGHEL, MAURICE DE. Les encres, les cirages, les colles et leur préparation. Paris 1922. pp. 384. ill. (*Recd.* 10/6/22.)

LEWKOWITSCH, JULIUS. Chemical technology and analysis of oils, fats, and waxes. 6th edition, revised by GEORGE H. WARBURTON. Vol. II. London 1922. pp. xii + 960. ill. 42*s*. net. (*Recd.* 25/5/22.)

MANN, JOHN DIXON. Forensic medicine and toxicology. 6th edition. Revised by WILLIAM A. BREND. London 1922. pp. xii + 574. ill. 30*s*. net. (*Recd.* 13/6/22.)

PROCTER, HENRY RICHARDSON. The principles of leather manufacture. 2nd edition. London 1922. pp. viii + 688. ill. 32*s*. net. (*Recd.* 13/6/22.)

REVUE DE METALLURGIE. Fondée avec concours de la Société d'Encouragement pour l'Industrie Nationale, du Comité des Forges de France et de différents établissements industriels. Vol. 16, etc. Paris 1919 +. (*Reference.*)

TUTTON, ALFRED EDWIN HOWARD. Crystallography and practical crystal measurement. 2 vols. [2nd edition.] London 1922. pp. xviii + 746 + xiv, viii + 747 to 1446. ill. £5 net. (*Recd.* 13/6/22.)

VALENTA, EDUARD. Photographische Chemie und Chemikalienkunde mit Berücksichtigung der Bedürfnisse der graphischen Druckgewerbe. Part I. Anorganische Chemie. 2nd edition. Halle (Saale) 1921. pp. xvi + 282. ill. (*Recd.* 31/5/22.)

ZERR, GEORG, and RÜBENCAMP, ROB. Handbuch der Farbenfabrikation. 3rd edition. Berlin 1922. pp. xvi + 908. ill. (*Recd.* 23/5/22.)

## III. *Pamphlets.*

BAILEY, E. H. S. A dietary study of some Kansas institutions under the control of the State Board of Health. Lawrence, Kansas 1921. pp. 70.

BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION. The Shirley Institute. [Didsbury] 1922. pp. 22. ill.

CANADIAN INSTITUTE OF CHEMISTRY. [History, etc.] Montreal [1922]. pp. 56. ill.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. Lecture on chemists and the patent laws. By HORATIO BALLANTYNE. London 1922. pp. 31.

MOIR, JAMES. Colour and chemical constitution. Part XIII. The calculation of the colour of the monocyclic dyes. Part XIV. The calculation of the colour of the dicyclic dyes. (From the *Trans. Roy. Soc. S. Africa*, 1921, **10**.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. Bulletin No. 6. On the electro-deposition of iron. With an appendix containing a bibliography on the subject. By WILLIAM EARL HUGHES. London 1922. pp. iv + 50. ill.

—— Deterioration of structures of timber, metal, and concrete exposed to the action of sea-water. Second (interim) report of the Committee of the Institution of Civil Engineers. Edited by P. M. CROSTHWAITE and GILBERT R. REDGRAVE. London 1922. pp. 57.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 5th, 1922, at 8 p.m., Sir JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of the following Fellows:

| | Elected. | Died. |
|---|---|---|
| Frederick Bedford .............. | June 20th, 1901. | July 13th. |
| Frederick Douglas Brown ...... | Mar. 20th, 1876. | Aug. 2nd. |
| William Kellner .................. | Mar. 19th, 1874. | Sep. 12th. |
| George William MacDonald ... | Dec. 6th, 1894. | Aug. 7th. |
| Alfred Ernest Moore ........... | June 17th, 1903. | Mar. 1st. |
| Arthur Faraday Price ........... | May 4th, 1882. | Mar. 17th. |
| Alexander Smith .................. | April 17th, 1890. | Sep. 8th. |
| Lionel William Stansell ......... | Feb. 3rd, 1887. | May 22nd. |
| James Stenhouse .................. | May 5th, 1892. | Mar. 18th. |
| Matthew Carrington Sykes ...... | Feb. 19th, 1891. | Aug. 25th. |
| Jokichi Takaminé .............. | Feb. 3rd, 1887. | July 22nd. |
| Stanley Goulden Thompson ... | May 1st, 1919. | Feb. 23rd. |
| James Waterhouse .............. | Feb. 7th, 1901. | Sep. 28th. |

In announcing the resignation of Dr. M. O. Forster from the office of Treasurer, the President referred to the many valuable services Dr. Forster had rendered to the Society during the past twenty years. His resignation was received with profound regret and his presence at the meetings would be greatly missed, and the President wished him, in the name of the Society, every success in the important work he was about to undertake as Director of the Institute of Science at Bangalore. Dr. Forster briefly responded.

It was stated that the Council had nominated Professor J. F. Thorpe, C.B.E., F.R.S., to fill the office of Treasurer until the date of the next Annual General Meeting, and that Dr. J. T. Hewitt, F.R.S., had been nominated to fill, for the same period, the vacancy amongst the Vice-Presidents caused by Professor Thorpe's appointment.

The President further announced that some time ago the *American Chemical Society* submitted to the Council certain proposals according to which we should be associated with them in the future conduct and control of the *Journal of Physical Chemistry*. Advantage was taken of the recent presence in this country of Dr. Parsons, Secretary of the American Chemical Society, to carry through the negotiations. The Council has to report that a satisfactory issue has been reached, the scheme having been widened to admit of the association of the Faraday Society with the enterprise. From some future date, probably January 1924, the *Journal of Physical Chemistry* will be accordingly issued under the auspices of the American Chemical Society, the Chemical Society, and the Faraday Society. The editorial board will consist of four American and four British representatives, together with an Editor-in-Chief appointed by these eight.

The following were formally admitted Fellows of the Chemical Society: J. P. Levy, F. M. Brewer, V. E. S. Swainson, and R. S. Colborne.

Certificates were read for the first time in favour of:

Robert Allanson, 10, Grosvenor Drive, New Brighton, Wallasey.
Thomas Cuthbert Allchin, M.B.E., E. C. Powder Co., Ltd., Longfield, Kent.
James Wilson Armit, M.A., The Manse, Monikie, Dundee.
Menghraj Choithram Bathija, B.A., Fitzwilliam Hall, Cambridge.
Donald Charles Broome, Disgwylfa, Penmaenmawr, Carnarvonshire.
Walter Ferguson Buist, B.Sc., 24, New Hall Lane, Clubmoor, Liverpool.
Stanley Robert Bult, 63, Addiscombe Road, Croydon.
Arthur Josiah Burford, 419, Edgware Road, Maida Vale, W. 2.
Katragadda Seshachalam Choudary, M.A., M.Sc., 71, Coral Merchant Street, George Town, Madras, India.
Elliott Martin Christie, M.Sc., 37, Lynwood Avenue, Dunedin, New Zealand.
Frederick Stanley Clarke, 64, Golders Manor Drive, N.W. 11.
Sydney George Cavigan, 22, Walker Street, Burton-on-Trent.
Edward Dance, B.Sc., Castle Inn, Sandal, Wakefield.
Milton Dewhurst, B.Sc., A.I.C., 1280, Warwick Road, Acocks Green, Birmingham.
Samuel Frederick Ford, 65, Abbotts Road, Southall.
John Masson Gulland, B.Sc., 11, Chester Street, Edinburgh.
Herbert Haigh, B.Sc., 211, Park Road, Barnsley.
Thomas Edward Hubbard, 9, Cunliffe Street, Pendleton, Manchester.
James Ernest Humphries, B.A., M.Sc., 29, St. John's Road, Newport, Mon.
John Huntley, The Villa, Burstwick, nr. Hull.
Sydney Alfred Hurren, M.C., 39, Upper Marylebone Street, W. 1.
Habib Iskander, Heliopolis, Cairo, Egypt.
Edgar Jones, 167, Upper Dale Road, Derby.
Jan Kalff, D.Chem., Nieuwe Prinsengracht 126, Amsterdam.
Shankar Nath Kapur, B.Sc., 11, George Square, Edinburgh.
William Dawson Lloyd, 42, Tavistock Road, Westbourne Park, W. 11.
Philip Patrick Lynch, B.Sc., Church Street, Timaru, New Zealand.

Francis Geoffrey Macalpine, B.Sc., Broad Oak, Accrington.
Frederick Henry McDowall, M.Sc., Knox College, Dunedin, New Zealand.
Kenneth McKenzie, Endrik, Hamilton Road, Cambuslang, Glasgow.
Archibald Roy Hammond Martin, B.A., 8, Kingsland Road, Worthing.
Dina Nath, c/o P. Lal, Esq., Vakil, Jullundhur City, Punjab, India.
Torkild Haastrup Nielsen, B.Sc., Siam Cement Co., Ltd., Bangsüe, Siam.
Hidejiro Nishikawa, 3, Hachimancho, Asakusa, Tokyo, Japan.
Joseph Edwards Pooley, 1, Margaretting Road, Manor Park, E. 12.
Nagendra Prasad, M.Sc., Ranchi, Behar & Orissa, India.
Edmund Brydges Rudhall Prideaux, M.A., D.Sc., F.I.C., 6, Arboretum Street, Nottingham.
James Robert Pound, M.Sc., 601*a*, Dana Street, Ballarat, Victoria, Australia.
Alfred Norman Douglas Pullen, The Larches, Greenham Common, Newbury.
Thomas Abraham Robertson, Sassafras, Rickard Road, Bankstown, N.S.W.
Burke Rushworth, 4, West Park Terrace, Healey, Batley, Yorks.
Gopal Singh, M.Sc., The Brij, Gawalmaudi, Lahore, India.
George Victor Smith, A.R.C.S., Westleigh, Eggington Road, Wollaston, Wellingborough.
Francis Wilbert Stoyle, M.Sc., 37, Kansas Avenue, Belfast.
Leslie Stuart Theobald, A.R.C.S., 3, Ennismore Avenue, Chiswick, W. 4.
William Thompson, B.Sc., Ravensworth, Cockton Hill, Bishop Auckland.
Laurence Barnett Timmis, M.Sc.Tech., A.I.C., 19, Trinity Marsh Lane, Waltham Cross.
Richard Truszkowski, B.Sc., Koszykowa 21, m-3, Warsaw, Poland.
Humphrey Terence Vincy, B.Sc., Bramerton, Blakebrook, Kidderminster.
Eric Richard Boraman Woodward, B.Sc., The Vicarage, Herne Bay, Kent.
William James Uglow Woolcock, C.B.E., M.P., 166, Piccadilly, W. 1.

The following papers were read:

"Cupric tetrammine nitrite and the corrosion of copper by aqueous solutions of ammonia and of ammonium nitrate." By H. Bassett and R. G. Durrant.

"The additive formation of four-membered rings. Part I. The synthesis and resolution of some derivatives of 1 : 3-diazidine." By C. K. Ingold and H. A. Piggott.

"Rates of reduction of nitro-groups by hydrogen in the presence of colloidal palladium, especially of nitrotoluene isomerides." By W. H. Patterson.

"A determination of the relative proportions of the isomerides in nitrotoluene or toluidine." By W. H. Patterson.

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Ordinary Scientific Meeting, Thursday, October 19th, 1922, at 8 p.m. Professor H. E. Armstrong, LL.D., F.R.S., Vice-President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of:

| | Elected. | Died. |
|---|---|---|
| Frederick Thomas Harry .................. | June 20th, 1908. | Sept. 14th, 1922. |
| Edmond Herbert Grove-Hills ........... | Feb. 15th, 1894. | Oct. 2nd, 1922. |

Mr. C. D. Thomas was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

Leslie Bains, B.A., B.Sc., A.I.C., 5, Carlton Road, Stroud Green, N. 4.
George Joseph Burrows, B.Sc., Chemical Department, The University, Sydney, N.S.W.
John Hardwick Long Champion, B.Sc., 41, Triangle West, Clifton, Bristol.
Norman Evers, B.Sc., F.I.C., The Cottage, Salisbury Avenue, Cheam, Sutton.
Joshua William Farmery, M.A., A.I.C., 56, Sheen Road, Richmond, Surrey.
Philip Henry Gifford, B.Sc., Boys' High School, Salisbury, Rhodesia.
Joseph Keith Matthews, M.A., Cedric House, Rainhill, Liverpool.
John Ewart Moss, M.Sc., 298, Franklin Road, Kings Norton, Birmingham.
Harry Ward, M.Sc., A.I.C., 28, Commercial Street, E. 1.

The following papers were read:

"The polarity of double bonds. An extension of the theories of Lapworth and Robinson." By T. M. Lowry.

"The theories of polarity in organic compounds." By J. Kenner.

"A model to illustrate the orbits of the electrons above the carbon atom." By W. E. Garner.

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## NOTICES.

The next Ordinary Scientific Meeting takes place on November 2nd, at 8 p.m., and an Informal Meeting will be held on November 16th, *after the conclusion of the formal business of the Ordinary Scientific Meeting at 8 p.m.*

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## RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December next. Application for Grants, to be made on forms obtainable from the Assistant Secretary, Chemical Society, Burlington House, W. 1, must be received on or before Friday, December 1st, 1922.

All persons who received Grants in December, 1921, or December of any previous year, whose accounts have not been closed by the Council, are reminded that reports must be returned by December 1st.

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## COLLECTIVE INDEX, VOL. VI (1913–1922).

Volume VI of the Collective Index will be published in two parts. Part I (Index to Authors) will be issued in 1923 and Part II (Index to Subjects) in 1924.

The price to Fellows who apply before *Christmas Day*, 1922, is £2 17*s*. post free. A remittance, made payable to Mr. S. E. Carr, must accompany the application in each case and should be sent to the Assistant Secretary, Chemical Society, Burlington House, W. 1. The price to Fellows who apply after December 25th, 1922, will be £3 7*s*.

Arrangements have been made by which cases in blue or maroon cloth for binding this Index in three volumes (Authors Index 1 vol. and Subject Index, 2 vols.) will be supplied for the sum of Seven Shillings. The binding will involve an additional charge of 2*s*. 3*d*. per volume. The total cost, therefore, of binding the Index in cloth will be 13*s*. 9*d*.

Fellows desiring to avail themselves of this offer should apply to Messrs. Gurney & Jackson, 33, Paternoster Row, London, E.C. 4, and also inform the Assistant Secretary, so that the necessary instructions may be given for the Index to be posted direct to the Publishers.

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## RUSSIAN FUND.

A further appeal has been issued on behalf of Russian Men of Science. In addition to donations of money to be devoted to purchasing requisite articles, gifts of clothing (which, if used, must be in good condition) and recent chemical literature will be welcome.

The Chemical Society will act as the receiving depôt, and cheques (made payable to Mr. S. E. Carr and crossed " Russian Fund "), together with parcels of clothing, boots, books, etc., should be addressed to the Assistant Secretary, Chemical Society, Burlington House, W. 1.

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List of Papers received between June 16th and October 19th, 1922 :

" Experiments on the synthesis of the polyacetic acids of methane. Part VII. The preparation of *methylidenetriacetic acid* and of methanetetra-acetic acid." By C. K. Ingold and L. C. Nickolls.

" An instance illustrating the effect of attached groups on the ease of formation of the *cyclo*pentanone ring." By J. P. C. Chandrasena and C. K. Ingold.

" The formation and stability of *spiro-compounds*. Part IX. The influence on stability of groups of high molecular weight." By S. F. Birch and J. F. Thorpe.

"The viscosity of cellulose. Part II. The lowering of the viscosity of cellulose by various reagents." By R. A. JOYNER.

"The constitution of polysaccharides. Part V. The yield of glucose from cotton cellulose." By J. C. IRVINE and E. L. HIRST.

"The action of solvents on coal. Part I." By S. R. ILLINGWORTH.

"Studies in the glucosides. Part I. The constitution of indican." By A. K. MACBETH and J. PRYDE.

"The alkylhydrazones." By O. L. BRADY and G. P. MCHUGH.

"The formation of bromine derivatives of carbon without the production of hydrogen bromide." By B. M. GUPTA and J. F. THORPE.

"Limits for the propagation of flame at various temperatures in mixtures of ammonia with air and oxygen." By A. G. WHITE.

"The molecular scattering of light in normal pentane." By R. VENKATESWARAN.

"Preparation and reactions of stannous oxide and stannous hydroxides." By F. W. BURY and J. R. PARTINGTON.

"Investigation of antimony metal from different sources. Indication of isotopes." By S. D. MUZAFFAR.

"The catalytic decomposition of formic acid on surfaces of platinum and silver." By H. C. TINGEY and C. N. HINSHELWOOD.

"Inorganic complex salts. Crystallographic and optical study. Part I." By I. E. KNAGGS.

"The formation of derivatives of tetrahydronaphthalene from $\gamma$-phenyl fatty acids. Part II." By A. STEVENSON and J. F. THORPE.

"*N*-Oximino-ethers. Part II. *N*-Aryl ethers of 2 : 4- and 2 : 6-dinitrobenzaldoxime." By F. BARROW, E. D. GRIFFITHS, and E. BLOOM.

"The nitro- and amino-derivatives of *o*- and *p*-methoxybenzoic acid and of $\alpha$- and $\beta$-methoxynaphthoic acid." By V. FROELICHER and J. B. COHEN.

"The addition of ethyl sodiocyanoacetate and ethyl sodiomalonate to ethyl muconate." By E. H. FARMER.

"A synthesis of pyrylium salts of anthocyanidin type." By D. D. PRATT and R. ROBINSON.

"The action of sodium methoxide and its homologues on benzophenone chloride and benzylidene chloride. Part III." By J. E. MACKENZIE.

"On diacetylacetone." By J. N. COLLIE and A. A. B. REILLY.

"The explosion of acetylene and nitrogen. Part II." By W. E. GARNER and K. MATSUNO.

"The applicability of a linear poisoning law to the catalytic decomposition of hydrogen peroxide." By E. B. MAXTED.

"Molecular weights in alcoholic solutions from the elevation of the flash point." By R. WRIGHT.

"Selective solubility shown by aqueous alcohol when acting as a solvent." By R. WRIGHT.

"Attempts to prepare red sulphide dyes. Part II. Mercaptan derivatives of azo-dyes." By E. R. WATSON and S. DUTT.

"The isolation of muscarine, the potent principle of *Amanita muscaria*." By H. KING.

"Researches on residual affinity and co-ordination. Part IX. Cobaltammine salts of the nitro-dyes." By G. T. MORGAN and H. J. S. KING.

"The mobility of symmetrical triad systems. Part I. The conditions which confer mobility on symmetrical open-chain systems terminated by phenyl groups." By C. K. INGOLD and H. A. PIGGOTT.

"Cevadine. Part I." By A. K. MACBETH and R. ROBINSON.

"Cyclic addition. Part I. The occurrence and reversibility of reactions in which cyclic structures are formed by the direct union of unsaturated linkages. Part II. The reaction between azomethines." By C. K. INGOLD and H. A. PIGGOTT.

"*iso*Propylstannonic acid and some of its derivatives." By J. G. F. DRUCE.

"Syntheses of alkylidenecyanoacetic acids and of substituted succinic acids. Part I. Acids containing aromatic residues." By A. LAPWORTH and J. A. McRAE.

"On crystalline glucose-ammonia and *iso*glucosamine." By A. R. LING and D. R. NANJI.

"The autoreductiou of sulphurous acid." By G. M. BENNETT.

"Researches on the conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus. Part I. The action of sodium on *o*-phenylenediacetic ester." By W. H. PERKIN and A. F. TITLEY.

"A method for the preparation of αββ-trialkylated glutaric acids." By G. A. R. KON and J. F. THORPE.

"The bromine compounds of phenanthrene. Part II." By H. HENSTOCK.

"The solubility of phenanthrene in various organic solvents." By H. HENSTOCK.

"The sorption of liquids by charcoal." By J. DRIVER and J. B. FIRTH.

"The equilibria in aqueous solutions of the alkali metal bisulphites." By E. C. C. BALY and R. A. BAILEY.

"Studies in the anthracene series. Part III." By E. DE B BARNETT, J. W. COOK, and H. H. GRAINGER.

"The solubilities of the alkaline formates and acetates in water.' By N. V. SIDGWICK and J. A. H. R. GENTLE.

"The solubility of the alkaline salts of benzoic and the hydroxy benzoic acids in water." By N. V. SIDGWICK and E. K EWBANK.

"The mechanism of the formation of benzoylbenzoin by treatmen of benzoylmandelonitrile with an alcoholic solution of sodiur ethoxide." By H. GREENE and R. ROBINSON.

"The oxime of mesoxamide (*iso*nitrosomalonamide) and som allied compounds. Part IV. The ethers of *iso*nitrosomalon anilide, and *iso*nitrosomalondimethylamide, and *iso*nitroso malondibenzylamide." By A. G. RENDALL and M. A. WHITE LEY.

"Researches on residual affinity and co-ordination. Part X Salicylatotetramminocobaltic salts and the constitution o oxonium compounds." By G. T. MORGAN and J. D. MAIN SMITH

"The cyanine dyes. Part VI. Dyes containing a quinoline an a benzothiazole nucleus. The thio*iso*cyanines." By W. T. K BRAUNHOLTZ and W. H. MILLS.

"The isomerism of the oximes. Part X. Cinnam- and nitro cinnam-aldoximes." By O. L. BRADY and C. D. THOMAS.

"The problem of substitution in the benzene nucleus and th Thomson-Lewis-Langmuir theory of co-valence." By R FRASER and J. E. HUMPHRIES.

"The constitution of soap solutions. Cetylsulphonic acid an other sulphonates." By M. H. NORRIS.

"Physical chemistry of the oxides of lead. Part VI. The anodi behaviour of lead and lead peroxide." By S. GLASSTONE.

"Use of paraformaldehyde (gaseous formaldehyde) and paraldehyd (gaseous acetaldehyde) in the synthesis of alcohols." B C. E. WOOD and F. SCARF.

"Rotatory dispersion of the esters of lactic acid. Normal ester Part I." By C. E. WOOD, J. E. SUCH, and F. SCARF.

"The solubility and volatility of 1 : 3 : 5-dinitrophenol." B N. V. SIDGWICK and T. W. J. TAYLOR.

"The labile nature of the halogen atom in organic compound Part V. The action of hydrazine on the halogen derivativ of some esters and *cyclo*hexanes." By E. L. HIRST and A. I MACBETH.

"Esters of the hydroxyalkylarylamines. Part I. Acid sulphur esters of the simple monohydroxyethylarylamines." By K. I SAUNDERS.

"Harmine and harmaline. Part VI. The synthesis of *n*-methyltetrahydroharmine and the constitution of harmaline and of the alkylated harmines." By W. O. KERMACK, W. H. PERKIN, and R. ROBINSON.

"Note on the decomposition of the dithiocarbazinates." By S. M. LOSANITCH.

"The interaction of aldehydes and ketones with thiocarbamides in the presence of acids. Part II." By J. TAYLOR.

"The preparation of methylguanidine, and of ββ-dimethylguanidine by the interaction of dicyanodiamide, and methylammonium and dimethylammonium chlorides respectively." By E. A. WERNER and J. BELL.

"Adsorption and catalysis in Fuller's earth." By E. K. RIDEAL and W. THOMAS.

"Quantitative reduction by hydriodic acid of halogenated malonyl derivatives. Part II. The *s.-tetra-substituted amides of* bromo- and chloro-malonic acid." By R. W. WEST.

"Amylases of the cereal grains—the 'insoluble' amylase of barley." By J. L. BAKER and H. F. E. HULTON.

"Reactivity of hydrogen atoms in methylene groups." By T. H. READE.

"The condensation of the aromatic *o*-amino-sulphonic acids with *iso*cyanic acid." By J. R. SCOTT and J. B. COHEN.

"Monothioethylene glycol." By G. M. BENNETT.

"The β-chlorovinylarsines." By F. G. MANN and W. J. POPE.

"Piperitone. Part IV. The interaction of *dl*-piperitone and semicarbazide, and the isolation of pure *dl*-piperitone." By J. READ and H. G. SMITH.

"The chlorination and bromination of the toluic acids and the preparation of the phthalaldehydic acids." By W. DAVIES and W. H. PERKIN.

"The isomerism of metallic oxides. Part I. Lead monoxide." By M. P. APPLEBEY and R. D. REID.

"The action of the chlorides of phosphorous on chlorodimethyldihydroresorcin." By L. E. HINKEL and W. D. WILLIAMS.

"On the movements of explosion waves in tubes of different shapes." By C. CAMPBELL.

"The chlorination of benzoyl chloride." By E. HOPE and G. C. RILEY.

"Ethyl α-cyano-β-methyl glutaconate and its methyl homologues." By E. HOPE.

"The addition of hydrogen cyanide to derivatives of glutaconic acid. Part I. The addition of hydrogen cyanide to ethyl-α-

cyano-β-methyl glutaconate and its homologues." By E. HOPE and W. SHELDON.

"The velocity of reaction in mixed solvents. Part III. The influence of temperature on the velocity of saponification of esters." By H. McCOMBIE, H. A. SCARBOROUGH, and R. H. SETTLE.

"The action of ferrous chloride on some organic hydrochlorides." By W. M. CUMMING.

"The form of the vapour-pressure curve at high temperature. Part I. The curve for lead." By C. K. INGOLD.

"The optical rotations of the sugars." By J. G. MALTBY.

"Heteromorphism of calcium sulphate. Alabaster and its synthesis." By M. COPISAROW.

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"On the interchange of alcohol radicles in esters. Part II." By A. SHIMOMURA and J. B. COHEN.

"Note on the reduction of thorium oxide by metallic tungsten." THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (C. J. SMITHELLS).

"γ-Methylfructoside." By R. C. MENZIES.

"The ultrafiltration of soap solutions: sodium oleate and potassium laurate." By J. W. McBAIN and W. J. JENKINS.

"Some new derivatives of methylstannonic acid; their bearing upon its constitution." By H. LAMBOURNE.

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"A modified methyl-orange indicator." By K. C. D. HICKMAN and R. P. LINSTEAD.

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"The system chromium trioxide–sulphur trioxide–water." By L. F. GILBERT, H. BUCKLEY, and I. MASSON.

"The constitution of acetone derivatives of glucose and fructose." By J. C. IRVINE and J. PATTERSON.

"The formation and properties of dithio-ketones ($R_2C\colon S\colon S$) and dithio-ether ($R_2S\colon S$). Part III." By K. G. NAIK and M. D. AVASARE.

"The constitution of the terpene present in the essential oil from *Andropogon Jwarancusa*, Jones." By J. L. SIMONSEN.

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"The solubility and volatility of the nitrobenzaldehydes." By N. V. Sidgwick and W. M. Dash.

"*The action of magnesium on symmetrical tetrachloro- and tetra-bromo-tetramethylmethane.*" By A. Fairbourne.

"The triazo-group. Part XXII. *Cinnamic acid chlorohydrin and its conversion into α-triazo-β-hydroxy-β-phenylpropionic acid.*" By M. O. Forster and W. B. Saville.

"A model to illustrate the orbits of the electrons about a carbon atom." By W. E. Garner.

"The labile nature of the halogen atom in organic compounds. Part VIII. The reduction of chloro- and bromo-trinitromethane and of tetranitromethane." By T. Henderson and A. K. Macbeth.

"*The condensation of 9 : 10-diaminophenanthrene with phenanthraquinone and other o-quinones.*" By S. Dutt and E. R. Watson.

"Studies in the β-phenylglutaric acid series. Part I. A possible basis of a new method for the determination of the relative distribution of the valencies of polyvalent elements." By J. G. Jackson and J. Kenner.

"A simplified method for the resolution into its optically active components of *sec.*-octyl alcohol (methyl-*n*-hexylcarbinol)." By J. Kenyon.

"Electro-synthesis of azelaic and thapsic acids." By M. Carmichael.

"Photocatalysis. Part III. The photosynthesis of naturally occurring nitrogen compounds from carbon dioxide and ammonia." By E. C. C. Baly, I. M. Heilbron, and H. J. Stern.

"The preparation of potassium and sodium arylsulphoniodo-amides." By E. Roberts.

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## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

Barker, Thomas Vipond. Graphic and tabular methods in crystallography as the foundation of a new system of practice: with a multiple tangent table and a 5-figure table of natural cotangents. London [1922]. pp. xvi+152. ill. 14*s*. net. (*Recd.* 3/10/22.) From the Author.

British Association for the Advancement of Science. A retrospect 1831—1921. By O. J. R. Howarth. London 1922. pp. viii+318. ill. (*Reference.*) From the British Association.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. Fourth report on colloid chemistry and its general and industrial applications. London 1922. pp. 382. 5*s*. 6*d*. net. (*Recd.* 15/9/22.)

From the Dept. of Scientific and Industrial Research.

CAIN, JOHN CANNELL. The manufacture of dyes. London 1922. pp. x+274. 12*s*. 6*d*. net. (*Recd.* 3/10/22.)

From Mrs. J. C. Cain.

DENHAM, HENRY GEORGE. An inorganic chemistry. London 1922. pp. viii+684. ill. 12*s*. 6*d*. net. (*Recd.* 5/7/22.)

From the Author.

FOOTE, PAUL D., and MOHLER, F. L. The origin of spectra. New York 1922. pp. 250. ill. $4.50. (*Recd.* 30/9/22.)

From the Publishers: The Chemical Catalog Company, Inc.

[FRITZ, JOHN.] The John Fritz Medal. [2nd edition. New York 1922.] pp. 128. ill. (*Recd.* 23/6/22.)

From the Board of Award.

GRIFFITHS, HUGH. Materials of chemical plant construction—non-metals. London 1922. pp. 64. ill. 3*s*. net. (*Recd.* 4/9/22.)

——. The general principles of chemical engineering design. London 1922. pp. 64. ill. 3*s*. net. (*Recd.* 4/9/22.)

From the Publishers: Messrs. Benn Brothers.

HALE, ARTHUR JAMES. Modern chemistry, pure and applied. Vol. V. London [1922]. pp. viii+280. ill. 16*s*. net. (*Recd.* 7/9/22.) From the Publishers: Messrs. Virtue & Co.

HENRICH, FERDINAND. Theories of organic chemistry. Translated from the revised 4th German edition of 1921 by TREAT BALDWIN JOHNSON and DOROTHY A. HAHN. New York 1922. pp. xvi+604. ill. 30*s*. net. (*Recd.* 9/10/22.)

From the London Publishers: Messrs. Chapman & Hall.

HOLMES, HARRY N. Laboratory manual of colloid chemistry. New York 1922. pp. xii+128. 10*s*. net. (*Recd.* 21/8/22.)

From the London Publishers: Messrs. Chapman & Hall.

IMPERIAL INSTITUTE. Indian Trade Enquiry. Drugs and tanning materials. Reports on cinchona bark and myrobalans. London 1922. pp. x+60. 4*s*. net. (*Recd.* 28/7/22.)

From the Director.

INTERNATIONAL BREWERS' CONGRESS. Report of the proceedings of the Second Congress held at Chicago, October 18—21, 1911: with an account of the Second International Barley and Hop Prize Exhibition, and brief history of the American Exposition of brewing machinery, materials, and products. Vol. I. Chicago 1912. pp. 642. (*Reference.*) From Mr. J. C. N. Eastick.

JOURNAL DE PHYSIQUE ET LE RADIUM. Vol. III., etc. Paris 1922+. (*For Circulation.*) From the Faraday Society.

Kolbe, Hermann [Editor]. Das chemische Laboratorium der Universität Marburg und die seit 1859 darin ausgeführten chemischen Untersuchungen nebst Ansichten und Erfahrungen über die Methode des chemischen Unterrichts. Braunschweig 1865. pp. 524. ill. (*Recd.* 21/8/22.) From Professor P. Phillips Bedson.

——. Das chemische Laboratorium der Universität Leipzig und die seit 1866 darin ausgeführten chemischen Untersuchungen. Braunschweig 1872. pp. xii+668. ill. (*Recd.* 21/8/22.)
From Professor P. Phillips Bedson.

Kraus, Charles August. The properties of electrically conducting systems including electrolytes and metals. New York 1922. pp. 416. ill. $4.50 net. (*Recd.* 21/8/22.)
From the Publishers: The Chemical Catalog Company, Inc.

Lewis, William. Commercium philosophico-technicum; or, the philosophical commerce of arts: designed as an attempt to improve arts, trades, and manufactures. London 1763. pp. iv+xviii+x+646+xiv. ill. (*Recd.* 30/9/22.)
From Mr. E. Gardner.

Lind, Samuel Colville. The chemical effects of alpha particles and electrons. New York 1921. pp. 182. ill. $3 net. (*Recd.* 21/8/22.)
From the Publishers: The Chemical Catalog Company, Inc.

Loeb, Jacques. Proteins and the theory of colloidal behaviour. New York 1922. pp. xii+292. ill. 15*s.* net. (*Recd.* 6/7/22.)
From the Publishers: The McGraw Hill Book Company.

Malan, H. L., and Robinson, A. I. The weighing and measuring of chemical substances. London 1922. pp. 64. ill. 3*s.* net. (*Recd.* 4/9/22.) From the Publishers: Messrs. Benn Brothers.

Ministry of Munitions and Department of Scientific and Industrial Research. Technical records of explosives supply. No. 7. Manufacture of nitric acid from nitre and sulphuric acid. London 1922. pp. vi+86. ill. 10*s.* 6*d.* net. (*Recd.* 20/7/22.)
From the Department.

Mitchell, Charles Ainsworth. Documents and their scientific examination, with especial reference to the chemistry involved in cases of suspected forgery, investigation of disputed documents, handwriting, etc. London 1922. pp. xii+216. ill. 10*s.* 6*d.* net. (*Recd.* 21/8/22.) From the Publishers: Messrs. C. Griffin & Co.

Oil and Colour Chemists' Association. Journal. Vol. V. etc. London 1922+. (*Reference.*) From the Association.

Partington, James Riddick, and Parker, Leslie Henry. The nitrogen industry. London 1922. pp. xvi+336. ill. 21*s.* net. (*Recd.* 4/10/22.)
From the Publishers: Messrs. Constable & Co.

Polskiego Towarzystwa Chemicznego. Roczniki Chemji. Vol. I. Warszawa 1921. (*Reference.*) From the Society.

Schlesischen Kohlenforschungsinstitut der Kaiser-Wilhelm-Gesellschaft in Breslau. Mitteilungen. Vol. I. Berlin 1922. pp. viii+180. ill. (*Recd.* 21/8/22.)
From the Publishers: Gebrüder Borntraeger.

Scientific and Industrial Research, Department of. *Food Investigation Board.* Special Report No. 7. The preservation of food by freezing with special reference to fish and meat: a study in general physiology. By Walter Stiles. London 1922. pp. 186. ill. (*Reference.*) 10*s*. net. From the Department.

Sears, George W. A systematic qualitative chemical analysis: a theoretical and practical study of analytical reactions of the more common ions of inorganic substances. New York 1922. pp. vi+120. 8*s*. 6*d*. net. (*Recd.* 21/8/22.)
From the London Publishers: Messrs. Chapman & Hall.

Simmonds, Charles. Alcohol in commerce and industry. London 1922. pp. xii+120. ill. 3*s*. net. (*Recd.* 15/9/22.)
From the Publishers: Sir Isaac Pitman & Sons.

Sinnatt, Frank Sturdy, and others. Coal and allied subjects: *a compendium of the first ten bulletins issued by the* Lancashire and Cheshire Coal Research Association. [1918—1921.] London [1922]. pp. viii+205. ill. 15*s*. net. (*Recd.* 9/10/22.)
From the Publishers: Messrs. H. F. & G. Witherby.

Swarts, Fred. Cours de chimie organique. 3rd edition. Bruxelles 1921. pp. vi+674. ill. (*Recd.* 3/10/22.)

——. Cours de chimie inorganique. 3rd edition. Bruxelles 1922. pp. vi+734. ill. (*Recd.* 3/10/22.)
From the Publisher: M. Maurice Lamertin.

Swindin, Norman. Pumping in the chemical works. London 1922. pp. 80. ill. 3*s*. net. (*Recd.* 4/9/22.)

——. The flow of liquids in pipes. London 1922. pp. 64. ill. 3*s*. net. (*Recd.* 4/9/22.)
From the Publishers: Messrs. Benn Brothers.

Taylor, Hugh Stott. Industrial hydrogen. New York 1921. pp. 210. ill. \$3.50 net. (*Recd.* 21/8/22.)
From the Publishers: The Chemical Catalog Company, Inc.

Tôhoku Imperial University. Technology reports. Vol. I., etc. Sendai 1920+. ill. (*Reference.*) From the University.

Tsao, Hui Chun, and Adolph, William H. A text-book of general chemistry. Based on McPherson and Henderson: A course in general chemistry. Shanghai 1922. pp. xxvi+653. [In Chinese.] From the Authors.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, held in the Lecture Hall of the Institution of Mechanical Engineers, on Thursday, October 26th, 1922, at 8 p.m., Sir JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

Sir William H. Bragg, K.B.E., F.R.S., delivered his Lecture entitled: "The Significance of Crystal Structure." A vote of thanks to the Lecturer, proposed by Professor J. Norman Collie, and seconded by Dr. A. E. H. Tutton, was carried with acclamation, acknowledgment being made by Sir William Bragg.

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Ordinary Scientific Meeting, Thursday, November 2nd, 1922, at 8 p.m., Professor J. F. THORPE, C.B.E., D.Sc., F.R.S., Treasurer, in the Chair.

Reference was made to the great loss the Society had sustained by the death, on October 28th, of Professor Alexander Crum Brown, who was elected a Fellow on December 5th, 1867. The Chairman referred to Professor Crum Brown's long connexion with the Society, of which he had served as President for two years and as Vice-President for thirty-three years, and to his many valuable contributions to the science of chemistry.

The following were formally admitted Fellows of the Chemical Society: R. A. Mallet and Owen Owen.

Certificates were read for the first time in favour of:

Leopold Louis Bacarese, 2, Stirling Road, Clapham Road, S.W. 9.
Nicholas Timothy Belaiew, C.B., 33, Elvaston Place, Queen's Gate, S.W. 7.
James Bell, 30, Trinity College, Dublin.
John Arnold Cranston, D.Sc., 14, Fernleigh Road, Newlands, Glasgow.
Hugh John Curnow, 22, Halfway Street, Sidcup.
Richard Victor Eaton, B.Sc., A.R.C.S., Lakeside, Seldown, Poole.
Roland Hall Griffith, B.A., 14, Bigwood Avenue, Hove.
Lucy Higginbotham, M.Sc., 57, Wilbraham Road, Chorlton-cum-Hardy, Manchester.
Svend Hald Lassen, Briarwood, Manorgate Road, Kingston-on-Thames.

Reginald Arthur McNicol, M.Sc., Birnam, Rotherfield Road, Carshalton.
Thomas Malkin, B.Sc., A.I.C., Golden Square, Warrington.
Thomas Trevor Potts, 60, Christ Church Square, Macclesfield.
George Clifford Riley, B.A., B.Sc., 15, Wellington Square, Oxford.
Oscar Walter Snow, B.A., Graeme's Bank, Hatch End.
Thomas John Wall, B.A., Northcote, Alexandra Road, Malvern.

The following papers were read :

"The solubility and volatility of the nitrobenzaldehydes." By N. V. Sidgwick and W. M. Dash.

"Investigations on the dependence of rotatory power on chemical constitution. Part XIII. The spatial configuration of the unbranched aliphatic chain." By R. H. Pickard, J. Kenyon, and H. Hunter.

"Investigations on the dependence of rotatory power on chemical constitution. Part XIV. The normal aliphatic ethers of *d*-β-octanol." By J. Kenyon and R. A. McNicol.

"Investigations on the dependence of rotatory power on chemical constitution. Part XV. The normal aliphatic ethers of *d*-methylbenzylcarbinol." By H. Phillips.

"Investigations on the dependence of rotatory power on chemical constitution. Part XVI. A new type of Walden inversion." By H. Phillips.

"Investigations on the dependence of rotatory power on chemical constitution. Part XVII. The di-*d*-β-octyl esters of the acids of the general formula $(CH_2)_n(CO_2H)_2$." By L. Hall.

"Orientation of the 1 : 4- and 1 : 5-dimethylglyoxalines. Mode of fission of 5-aminoglyoxalines." By F. L. Pyman.

"Bromo-derivatives of 2-methylglyoxaline." By L. Light and F. L. Pyman.

"2 : 5-*Iminodihydro*-1 : 2 : 3-*triazole*. Part I. Constitution of Dimroth's 5-anilidotriazole." By P. K. Dutt.

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Unveiling Ceremony of the War Memorial to Lt.-Colonel E. F. Harrison, C.M.G., and other Fellows of the Chemical Society on Thursday, November 16th, 1922, at 3 p.m.

A report of the proceedings of the meeting will appear in the December issue of the Journal.

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Ordinary Scientific Meeting, Thursday, November 16th, 1922, at 8 p.m., Professor J. C. Philip, O.B.E., D.Sc., F.R.S., Secretary, in the Chair.

Reference was made to the loss sustained by the Society, through death, of the following Fellows :

| | Elected. | Die |
|---|---|---|
| Edward Henry Grossmann ........................ | Dec. 5th, 1895. | Aug. |
| Leo Tschugaeff ........................................ | Dec. 1st, 1910. | Sept. |

Messrs. J. R. Green and T. Iredale were formally admi Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

Kenneth Claude Bailey, M.A., 137, South Circular Road, Dublin.
Katherine Hope Coward, M.Sc., 14, Parliament Hill, Hampstead, N.W. 3.
Allan Robert Earle, B.A., 90, Shadwell Road, Portsmouth.
Samuel Gray Fenton, 27, Somerset Road, Harrow.
Phillip Marcus Fisk, 92, Aldborough Road, Seven Kings, Ilford.
Thomas Graham, 47, Canada Road, Cardiff.
Leslie Frank Hewitt, B.Sc., A.I.C., 8, Maze Road, Kew, Surrey.
John Ingham, 19, Greyhound Road, Tottenham, N. 17.
Wilfred Herbert Linnell, B.Sc., A.I.C., 12, Highbury, Monkseaton, Whitley Bay.
Ramprasad Pitamberdas Mahta, M.A., Organic Chemistry Dept., University College, Gower Street, W.C. 1.
Jocelyn Patterson, Ph.D., M.Sc., 106, Market Street, St. Andrews.
Tara Chand Rana, M.Sc., III Bridge, Srinagar, Kashmir, India.
John Baldwin Shoesmith, M.Sc., 10, Spottiswoode Road, Edinburgh.
Reginald Ernest Tebbit, 120, Lordship Lane, E. Dulwich, S.E. 22.
Eric Wilfred Tong, B.Sc., A.R.C.S., Hollingbourne, Maidstone.
Thomas Arthur Williams, Ridgeway House, Mill Hill, N.W. 7.

A Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of: Babu Lall Govila, Central Polytechnic Institute, Gwalior.

The meeting was then adjourned and the Informal Meeting declared open.

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List of Papers received between October 20th and November 16th, 1922:

"Investigations on the dependence of rotatory power on chemical constitution. Part XIII. The spatial configuration of the unbranched aliphatic chain." By R. H. Pickard, J. Kenyon, and H. Hunter.

"Investigations on the dependence of rotatory power on chemical constitution. Part XIV. The normal aliphatic ethers of *d*-β-octanol." By J. Kenyon and R. A. McNicol.

"Investigations on the dependence of rotatory power on chemical constitution. Part XV. The normal aliphatic ethers of *d*-methyl benzylcarbinol." By H. Phillips.

"Investigations on the dependence of rotatory power on chemical constitution. Part XVI. A new type of Walden inversion." By H. Phillips.

"Investigations on the dependence of rotatory power on chemical constitution. Part XVII. The di-*d*-β-octyl esters of the acids of the general formula $(CH_2)_n(CO_2H)_2$." By L. HALL.

"Orientation of the 1 : 4- and 1 : 5-dimethylglyoxalines. Mode of fission of 5-aminoglyoxalines." By F. L. PYMAN.

"Bromo-derivatives of 2-methylglyoxaline." By L. LIGHT and F. L. PYMAN.

"The oxidation of cane sugar by nitric acid." By F. D. CHATTAWAY and H. J. HARRIS.

"Castelamarin—a bitter principle from *Castela Nicholsoni*." By L. P. BOSMAN.

"Catalytic hydrogenation with nickel. Factors determining catalytic activity." By R. THOMAS.

"2 : 5-Iminodihydro-1 : 2 : 3-triazole. Part I. Constitution of Dimroth's 5-anilidotriazole." By P. K. DUTT.

"The action of alcohol on the sulphates of ammonium." By H. B. DUNNICLIFF.

"Refraction and dispersion of potassium vapour." By A. L. NARAYAN and G. SUBRAHMANIAM.

"The interaction of diazonium salts and phenols." By F. D. CHATTAWAY and H. R. HILL.

"The relation between the crystal structure and constitution of carbon compounds. Part I. Compounds of the type $CX_4$." By I. E. KNAGGS.

"Binary critical solution temperatures as criteria of the purity of acetic acid." By D. C. JONES.

"Ternary critical solution temperatures as a criterion of liquid purity." By D. C. JONES.

"Syntheses of alkylidenecyanoacetic acids and of substituted succinic acids. Part II. Preparation of acids containing saturated aliphatic residues and the constitution of the aliphatic alkylidenecyanoacetic esters." By A. LAPWORTH and J. A. McRAE.

"Formation of γ-alkylidene derivatives from ethylidenemalonic ester." By A. LAPWORTH and L. HIGGINBOTHAM.

"Resorcinolphenylsuccinein." By A. LAPWORTH and J. A. McRAE.

"The preparation of α-trioxymethylene and a new polymer of formaldehyde." By D. L. HAMMICK and A. R. BOEREE.

"The isoelectric condition of gelatin." By S. O. RAWLING and W. CLARK.

"The nitration of 3-chloroacenaphthene." By G. FARNELL.

"The diazo-reaction in the carbazole series. Carbazole-3-diazoimine and -3-diazonium salts." By G. T. MORGAN and H. N. READ.

"The oxidation of sabinene with chromyl chloride." By G. G. HENDERSON, J. M. ROBERTSON, and D. C. BROWN.

"Scattering of light by $CO_2$ and $N_2O$, and by some organic vapours." By A. L. NARAYAN.

"1:3:4:6-Tetramethyl fructose." By J. C. IRVINE and J. PATTERSON.

"Researches on residual affinity and co-ordination. Part XII. Interactions of metallic salts and dimethyldithiolethylene." By G. T. MORGAN and W. LEDBURY.

"Researches on residual affinity and co-ordination. Part XIII. Cobaltammine and ferric lakes of dinitrosoresorcinol." By G. T. MORGAN and J. E. MOSS.

"Researches on residual affinity and co-ordination. Part XIV. Cobaltammine and cobaltic lakes of the azo-salicylic acids." By G. T. MORGAN and J. D. M. SMITH.

"Boundary lubrication and chemical constitution. The optically active carbinols of the formula $C_2H_5{\cdot}CH(OH){\cdot}C_nH_{2n+1}$." By I. DOUBLEDAY.

"The velocity of reaction in mixed solvents. Part IV. The influence of the base on the velocity of saponification of esters." By A. CASHMORE, H. McCOMBIE, and H. A. SCARBOROUGH.

"The adsorption of radium-*B* and radium-*C* by ferric hydroxide." By J. A. CRANSTON.

"The hydrolysis of platinum salts. Part II. Potassium platinichloride." By E. H. ARCHIBALD and W. A. GALE.

"On the reactivity of methyl groups in heterocyclic bases." By W. H. MILLS and J. L. B. SMITH.

"An examination of the reputed antimonious hydroxides." By C. LEA and J. K. WOOD.

"The adsorption of stannous chloride by stannic acid." By G. E. COLLINS and J. K. WOOD.

"The composition of paraffin wax. Part III." By F. FRANCIS, C. M. WATKINS, and R. W. WALLINGTON.

"The hydrogen sulphates of the alkali metals and ammonium." By H. B. DUNNICLIFF.

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## LECTURE.

On Thursday, December 14th, at 8 p.m., at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1, Professor Cecil H. Desch, D.Sc., Ph.D., will deliver a Lecture entitled "The Metallurgical Applications of Physical Chemistry."

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## COLLECTIVE INDEX, VOL. VI (1913–1922).

Volume VI of the Collective Index, to be published in two parts, will be issued Part I in 1923 and Part II in 1924.

The price to Fellows who apply before *Christmas Day*, 1922, is £2 17*s*. *post free. A remittance, made payable to* Mr. S. E. Carr, *must accompany the application in each case and should be sent* to the Assistant Secretary, Chemical Society, Burlington House, W. 1. The price to Fellows who apply after December 25th, 1922, will be £3 7*s*.

Arrangements have been made by which cases in blue or maroon cloth for binding this Index in three volumes (Authors' Index, 1 vol. and Subject Index, 2 vols.) will be supplied for the sum of Seven Shillings. The binding will involve an additional charge of 2*s*. 3*d*. per volume. The total cost, therefore, of binding the Index in cloth will be 13*s*. 9*d*.

Fellows *desiring to avail themselves of this offer should apply* to Messrs. Gurney & Jackson, 33, Paternoster Row, London, E.C. 4.

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## CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, DECEMBER 7TH, 1922.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

ALLANSON, ROBERT, "Oaklands," 10, Grosvenor Drive, New Brighton Wallasey, Cheshire. British. Director of Powell & Scholefield, Ltd. Chemical Manufacturers, Liverpool, and interested in research on behal of the chemical industry and in connexion with manufacturing chemistry (*Signed by*) R. L. Siau, Arnold R. Tankard, Douglas Henville.

ALLCHIN, THOMAS CUTHBERT, (M.B.E.), Longfield, Kent. Works manage (chemical), E. C. Powder Coy., Ltd. Manufacturing chemistry. To receiv publications and attend meetings. (*Signed by*) Edgar Neumann, Matthew J Cannon, Herbert E. Burgess.

ARMIT, JAMES WILSON, The Manse, Monikie, nr. Dundee. Chemical researc student at St. Andrew's University. M.A., St. Andrews (1920). Researc student in chemistry since October 1921. (*Signed by*) Robert Robinson J. C. Irvine, John Pryde, E. L. Hirst.

BACARESE, LEOPOLD LOUIS, 2, Stirling Road, Clapham Road, S.W. British. Managing Chemist. (1) Two years student at the Westminst School of Pharmacy, London, S.W. (2) Passed the qualifying exam Gibraltar. (3) Member of the Pharmaceutical Society. (4) Member of th British Optical Association and the Institute of Ophthalmic Opticiar (5) Four years Managing Chemist to Heppell & Co., London. Keenly desiro of becoming a Fellow to keep in touch and attend lectures, receive Society publications, with a view to improving experience in Organic Chemistr

(*Signed by*) Robert S. Glennie, W. Bennison, P. H. Woodnoth, H. Sampson Wills.

BAINS, LESLIE, 5, Carlton Road, Stroud Green, N.4. British. Research Student. Natural Sciences Tripos, Cambridge: Part I (1st Class), Part II (2nd Class). Two years' research in Organic Chemistry at Cambridge; now at the Imperial College of Science, South Kensington. B.A. (Cantab.), B.Sc. (London). Associate of Institute of Chemistry. (*Signed by*) Jocelyn Thorpe, C. K. Ingold, Arnold Stevenson, G. A. R. Kon.

BATHIJA, MENGHRAJ CHOITHRAM, Fitzwilliam Hall, Cambridge. British subject. Student. I have remained as a student of chemistry for the last six years at the universities of Bombay and Cambridge, respectively, and have obtained Honours degree of Bombay in chemistry and physics, and 2nd Class Honours degree of Cambridge in chemistry, physics, and botany. (*Signed by*) H. J. H. Fenton, A. J. Berry, T. M. Lowry.

BELAIEW, NICHOLAS TIMOTHY, Colonel, C.B., 33, Elvaston Place, Queen's Gate, London, S.W.7. Russian. Metallurgist. Formerly Lecturer in Chemistry and Metallurgy at the Michael Artillery Academy, Petrograd. Colonel, C.B., M.I.Met., M.I.Min.E., Hon. M.I.Ae.E. Honorary Corresponding Fellow of the Royal Society of Arts. Honorary Corresponding Member of the Council of the Institute of Metals. Member of the Council of the I. Aeronautical Engineers. Member of the Iron and Steel Institute, the Faraday Society, the Society of Chemical Industry, and of the Mineralogical Society. *Member of the Société de Chimie Physique in Paris.* In Russia member of Society of Physics and Chemistry, Imp. R. Mineralogists and others. Contribntor of several papers on chemistry, physics, and crystallography. (*Signed by*) H. C. H. Carpenter, W. J. Pope, R. A. Hadfield.

BELL, JAMES, 30, Trinity College, Dublin. British. University Demonstrator of Chemistry. Senior Moderator in Experimental Science (with large gold medal for first place and high marks), Dublin University, 1920. Demonstrator of chemistry, Dublin University, 1919–1922. Part author of two papers on original research, viz. *J. Chem. Soc.*, **117**, 1133, (1920), and *J. Chem. Soc.*, **121**, 1790, (1922). (*Signed by*) Sydney Young, Emil A. Werner, A. G. G. Leonard.

BROOME, DONALD CHARLES, "Disgwylfa," Penmaenmawr, North Wales. British. Technical Chemist. Educated at Emanuel School, Wandsworth Common, and later at Woolwich and Battersea Polytechnics. Have passed Inter. B.Sc. (London) and am studying for final B.Sc., having completed one year's work for this examination. Late chief assistant chemist at the South Met. Gas Co.'s Tar Works, East Greenwich. Now holding the post of works chemist at the Penmaenmawr works of the Penmaenmawr and Trinidad Lake Asphalt Co., Ltd. (*Signed by*) M. O. Forster, J. Kenyon, J. L. White, Herbert E. Nickels, *Wallace C. Nickels.*

BUIST, WALTER FERGUSON, 24, New Hall Lane, Clubmoor, Liverpool. Scotch. Graduate. Awaiting teaching post. Northern Universities Matriculation 1913. Inter.B.Sc., University of Liverpool, 1914. (War service 1914–1920.) Honours chemistry, B.Sc., 1922. Desirous of keeping in touch with current literature. (*Signed by*) E. C. C. Baly, Herbert H. Froysell, I. M. Heilbron, J. S. Buck.

BULT, STANLEY ROBERT, 63, Addiscombe Rd., Croydon. British. Chemist. At present time Curator, Institute of Hygiene, lecturing and demonstrating upon dietetic and hygienic problems. Twenty-two years' experience of chemistry (with break during the war). Seventeen years' laboratory work, oils, waxes, soaps, paints, metals, rubber, foodstuffs. Some

*small contributions to technical journals.* (*Signed by*) Herbert J. Bult, Lawrence Briant, Julian L. Baker.

Burford, Arthur Josiah, c/o 419, Edgware Rd., Maida Vale, W.2. British. Chemist and Druggist. (1) Two years student in chemistry at the School of Pharmacy of the Pharmaceutical Society, Bloomsbury Square, W.C. (2) One year student in pharmaceutical and analytical chemistry at the London College of Chemistry and Botany, S.W. (3) Member of the Pharmaceutical Society. (4) Three years laboratories of Wands, Manufacturing Chemists, Leicester. (5) Three years chemist to Heppell & Co., London. (6) Keenly desirous of becoming a Fellow to keep in touch and attend lectures, receive Society's publications, with a view to improving experience in Pharmaceutical Organic Chemistry. (*Signed by*) William Bennison, Gabriel Cofman-Nicoresti, Robert S. Glennie.

Burrows, George Joseph, Chemical Department, University, Sydney N.S.W. B.Sc. Sydney (1910). Lecturer in Chemistry, Sydney University Author of various publications in *J.C.S.* since 1914. (*Signed by*) Eustace E Turner, Charles E. Fawsitt, J. A. Schofield.

Carter, William Leslie, "Ellesmere," Bloxcidge St., Langley Green nr. Birmingham. British. Works Chemist (in charge). Educated at the Secondary School, Oldbury (by county scholarship). Oxford Univ. local exam. honours and distinction in chemistry. 1915, Assistant chemist Messrs. Chance & Hunt, Ltd., Oldbury, Chemical Mfrs. 1916, Assistant chemist, Messrs. J. Hardman, Ltd., Birmingham, tar distillers. 1917, Assistant chemist, H.M. factory site "B," Oldbury. 2½ years' military service (France). 1921, Board of Education higher education course in advanced chemistry. 1922, Chemist-in-charge, Messrs. Birmingham Starch & Mfg. Co., Ltd., Birmingham. Paper in preparation on "The Manufacture of Starch." (*Signed by*) J. G. Howarth, Arthur Adams, Joseph Lones.

Cavigan, Sydney George, 22, Walker St., Burton-on-Trent. Analytical Chemist. I have had five years' experience in the analysis of metals, foods and drugs, and general experience in biological chemistry and toxicology and am at present in charge of the analytical department of Messrs. Evans Sons, Lescher & Webb, Research Laboratories, Runcorn. I wish to become a member in order to obtain the *Journal* to assist me in my researches, and to keep up my knowledge of modern chemical literature. (*Signed by*) Wm. P Skertchly, James Booth, J. Turnbull, Herbert H. H. Lorenz.

Champion, John Hardwick Long, 41, Triangle West, Clifton, Bristol Student. Bachelor of Science (Bristol). Have done eight months' research in physical chemistry under Prof. J. W. McBain. Am at present engaged as a part-time teacher of chemistry and physics. (*Signed by*) J. W. McBain M. Nierenstein, Millicent Taylor, B. Fullman.

Choudary, Katragadda Seshachalam, 71, Coral Merchant St., George Town, Madras, India. Indian (Hindu). Leather Trades Chemist. Master of Arts of the University of Madras, Master of Science of the University of Leeds; lecturer in chemistry in the Christian College, Madras (1917–18); lecturer in chemistry in the Government Arts College, Rajahmundry, Madras (1918–19); chemist in the Leather Trades Institute, Madras (1919–20). (*Signed by*) P. K. Dutt, Akira Shimomura, H. M. Dawson.

Christie, Elliot Martin, 37, Lynwood Avenue, Dunedin, N.Z. Secondary School Teacher. Graduated B.Sc., Victoria University College, 1920. M.Sc. (2nd Class Honours in Chemistry), 1922. Thesis on "Oxidation of Unsaturated Organic Compounds by Persulphate." Appointed Science Master, Gore High School, 1922. (*Signed by*) J. K. H. Inglis, John Williams, C. S. Hicks.

Clarke, Frederick Stanley, 64, Golders Manor Drive, N.W.11. British Pharmaceutical Chemist. 1899, Demonstrator (chemistry and pharmacy), Manchester. From 1900, 2½ years with the late Wm. Martindale, editor *Extra Pharmacopœia*. 1902 to 1920 on technical experimental staff, Burroughs, Wellcome & Co., London. At present works manager and chemist Anglo-American Oil Co.'s Speciality Dept. for petroleum products. (*Signed by*) Harold King, Harold C. Sayer, Frank Lee Pyman.

Cottrell, Allin, 3, Oxford Terrace, Edinburgh. British. Lecturer in Technical Chemistry, Edinburgh University. Lately chief chemist, H.M. Factory, Gretna. (*Signed by*) James Walker, Sydney A. Kay, Leonard Dobbin

Cranston, John Arnold, 14, Fernleigh Road, Newlands, Glasgow. British Lecturer on Physical Chemistry, Royal Technical College, Glasgow. Doctor of Science, Glasgow University. Lecturer in Royal Technical College for three years. (*Signed by*) F. J. Wilson, Thomas Gray, R. M. Caven.

Curnow, Hugh John, 22, Halfway St., Sidcup. English. Undergraduate Inter. Science (London). Student of the Institute of Chemistry. (*Signed by*) H. Pochin, J. R. Partington, W. H. Patterson.

*Dance, Edward, Castle Inn, Sandal, Wakefield. British. Student* B.Sc. Hons. in Col. Chem., Leeds, and Diploma in Dyeing, Leeds University Desire Fellowship in order that I may receive the *Journal* and have use of Library. (*Signed by*) R. M. Woodman, J. R. Scott, P. W. Clutterbuck John S. Carter.

Davies, Wilfred Thomas Grey, Plas-y-Coed, Derllwyn Rd., Tondû Glamorgan. British. Assistant, Tondû By-product Works. B.Sc., Bristol 1920. Inter.B.Sc., 1914. Carried out research under Dr. M. Nierenstein at Bristol University. (*Signed by*) M. Nierenstein, M. Taylor, F. Francis J. W. McBain, B. Fullman.

Dewhurst, Milton, 1280, Warwick Rd., Acocks Green, Birmingham British. Works Chemist. *B.Sc. Hons. Chemistry (Vict.).* A.I.C. (*Signed by*) H. B. Dixon, Arthur Lapworth, F. P. Burt, Frederick Challenger, John Harwood.

Eaton, Richard Victor, "Lakeside," Seldown, Poole. British. Chemist R.N. Cordite Factory. A.R.C.Sc., B.Sc. (Lond.). (*Signed by*) H. B. Baker M. A. Whiteley, James C. Philip.

Evers, Norman, The Cottage, Salisbury Avenue, Cheam, Surrey. British Chemist. B.Sc. (London), F.I.C. Chief chemist to Messrs. Allen & Hanbury's Ltd., Bethnal Green, E.2. Author of numerous papers on chemical subjects published in the *Analyst* and elsewhere. (*Signed by*) F. W. Gamble, G. J. Woods, Thos. McLachlan.

Farmery, Joshua William, 56, Sheen Rd., Richmond, Surrey. British Analytical and Research Chemist. M.A. (Cantab.). A.I.C. Research paper "Decomposition of Nitric Esters," by Lowry, Browning, and Farmery *J.C.S.* (*Signed by*) T. M. Lowry, A. F. Joseph, Cecil H. Cribb.

Ford, Samuel Frederick, 65, Abbotts Road, Southall, Middlesex British. Assistant Chemist. (Analysis of oils, essences, and foods Assistant for three years in laboratory of rubber and antimony manufacture Now assistant chemist in laboratory of food manufacturers. Ex-day and now evening student at Battersea Polytechnic. Studying for Science degree Rutlish Secondary School, Merton, Old Boy. (*Signed by*) F. J. Wilson G. S. W. Marlow, J. Beauchamp Salter.

Gardner, Roy, 91, Lincoln Rd., Masterton, N.Z. Honours Student (Chemistry), University College, Otago, N.Z. Desirous of keeping in touch with recent developments. B.Sc. (N.Z.), now doing research work in chemistry

at Univ. of Otago, N.Z. (*Signed by*) Fredk. P. Worley, W. F. Short, A. E Bowell, J. K. H. Inglis, Thomas H. Easterfield.

GIFFORD, PHILIP HENRY, Boys' High School, Salisbury, S. Rhodesia, S Africa. Science Master. B.Sc. (Vict.) (1st Class Chemistry and Physics) Assistant Science Master, Ballymena Academy, Co. Antrim (1913–14 Senior Science and Maths. Master, Edinburgh Institution (1914–17 and pa of 1919). Senior Science Master and Vice-Principal of the Boys' High Schoo Salisbury, S. Rhodesia, from Jan. 1st, 1920. (*Signed by*) Charles A. Fogg T. M. Nightingale, E. Boardman.

GRIFFITH, ROLAND HALL, 14, Bigwood Avenue, Hove, Sussex. British B.A. (Chemistry), Oxford. Engaged on research in organic chemistry a the University laboratories. (*Signed by*) Edward Hope, W. H. Perkin S. G. P. Plant, Allan F. Walden, N. V. Sidgwick, M. P. Applebey, F Lambert.

GRIFFITHS, REGINALD WILLIAM, 137, Holly Road, Handsworth, Birmingham Member of Research Staff, Research Laboratory, Dunlop Rubber Co., Ltd Fort Dunlop, Birmingham. Research student at Birmingham Municipa Technical School. B.Sc. (Birmingham), 1920. (*Signed by*) J. Newton Friend Frederick Challenger, J. E. Coates, S. R. Carter, G. T. Morgan.

GULLAND, JOHN MASSON, 11, Chester Street, Edinburgh. Chemical Researc Student. B.Sc. in pure science, Edinburgh University, July 1921. Researc student, Chemistry Department, University of St. Andrews. (*Signed by* Robert Robinson, J. C. Irvine, John Pryde, E. L. Hirst.

HAIGH, HERBERT, 211, Park Road, Barnsley, Yorkshire. British Student (Graduate). Alternative Matriculation for ex-service men, 1919 Inter. B.Sc., Liverpool, 1920, Maths., Physics, and Chemistry. B.Sc. Liver pool, 1922, Honours Chemistry, Class I. Desirous of keeping in touch wit current literature. (*Signed by*) I. M. Heilbron, E. C. C. Baly, Herbert E Froysell, Harold Rogerson, J. S. Buck.

HIGGINBOTHAM, LUCY, 57, Wilbraham Rd., Chorlton-cum-Hardy, Man chester. British. Research Assistant in Organic Chemistry at the Britis Cotton Research Association, Didsbury. B.Sc., Honours Chemistry, 1s Class, 1919, at Manchester University. M.Sc., 1920. Working for Dr. Stephen at Manchester University. 1921–22 Private assistant to Professor Lapworth Publications: "The Formation of Substituted Succinic Acid from Ester of αβ-Unsaturated Esters," by Arthur Lapworth and Lucy Higginbotham "Studies in the Coumaranone Series. Part I," by Lucy Higginbotham an Henry Stephen. (*Signed by*) Arthur Lapworth, Frederick Challenger, Lesli R. Ridgway, R. G. Fargher.

HUBBARD, THOMAS EDWARD, 9, Cunliffe Street, Pendleton, Manchester Senior Assistant Chemist to the Salford Corporation Gas Works. As a student at the College of Technology, Salford, gained numerous prizes an scholarships in chemistry. Deputised for Mr. C. E. Teasdale, lecturer o gas manufacture. Lectured on calorimetry in modern gas works practice etc. (*Signed by*) Jas. Grant, E. Bayley, Frank B. Small.

HUMPHRIES, JAMES ERNEST, 29, St. John's Rd., Newport, Mon. British University Assistant in Chemistry, Aberdeen. B.A. (Lond. and Cantab.) M.Sc. (Wales). (*Signed by*) W. Thomas, E. Bloom, F. G. Mann.

HUNTLEY, JOHN, The Villa, Burstwick, nr. Hull. Works Chemist. Chie chemist, Humber Portland Cement Co., Ltd., Melton, East Yorks. (*Signe by*) W. H. Coates, Harry Thompson, Thos. A. Nightscales, E. B. Atkinso T. Luxton.

HURREN, SYDNEY ALFRED, M.C., 39, Upper Marylebone St., W.1. Britis

Lecturer at Northern Polytechnic Institute on Technology of Pianoforte Construction, and technical editor of *The Pianomaker*, the monthly journal of the trade. (*Signed by*) Thomas J. Drakeley, *Philip Schidrowitz*, Raymond R. Butler.

Iskander, Habib, Heliopolis, Cairo. Egyptian. Senior Science Master of the American University, Cairo, Intermediate Section. Graduate of Royal Training College, Cairo, with top mark in chemistry, 1915. Late Senior Chemistry Master at Victoria College, Alexandria, 1915–21. (Victoria College is an English College qualifying for the Oxford and Cambridge Schools Examinations.) Author of "Khoulasit Al Chemia," an Arabic text-book in chemistry adopted by many schools and colleges. Contributor of some articles on "Recent Advances in Chemical Science" published in *Al Moktataf*, the biggest scientific magazine in the Arabic-speaking world. (*Signed by*) A. I. Kahil, A. H. Ahmad, W. Morris Colles, R. Fleming.

Jenkin, John Watson, "Tregardock," St. Austell, Cornwall. Metallurgical Research Chemist. B.Sc. (Hons.) London (2nd Class Hons. in Chemistry). A.I.C. (by examination). Studied chemistry at King's College, London, under Professors Crossley, Smiles, and Allmand. At present engaged in research work under Professor C. H. Desch in the Dept. of Metallurgy, University of Sheffield. (*Signed by*) Cecil H. Desch, A. J. Allmand, Samuel Smiles.

Jewell, John Ernest, 34, Grove End Road, St. John's Wood, N.W.8. English. Pharmaceutical Chemist. Proprietor of Messrs. Heppell, West-end chemists. Member of the Pharmaceutical Society. Director of many well-known chemical firms. (*Signed by*) Frank Radcliffe, Stanley J. Peachey, C. S. Gibson.

Jones, Edgar, *Milverton House, 167, Upper Dale Road*, Derby. Technical Chemist. Chief chemist, Derby Gas Light & Coke, Co. Late chemist Gas Helmet Redipping Station, R.A.O.D., Alexandria. Inter. B.Sc. (London). Lecturer, Gas Engineering and Manufacture, Derby Technical College. (*Signed by*) Jos. Yates, Cyril H. Birkitt, Stanley Dixon.

Kalff, Jan, Amsterdam, Nieuwe Prinsengracht 126. Dutch. Assistant, University, Amsterdam. Chem. Doct. Engaged in organic chemical work. Desire to keep up with the latest English investigations in chemistry. (*Signed by*) H. J. Backer, W. A. Frederikse, F. G. Donnan.

Kapur, Shankar Nath, Amritsar, India (at present, 5, Grosvenor Crescent, Edinburgh). Distillery Chemist, Amritsar Distillery Co., Amritsar, India. B.Sc. Ist Class Honours in Chemistry from Government College, Lahore (Punjab University). Chemist to the Amritsar Distillery Co., Amritsar, India (from May 1917). Now sent by the Government of India to study "Industrial Alcohol" in England and on the Continent. (*Signed by*) John E. Mackenzie, Thomas H. Pope, B. H. Wilsdon, *Bawa Kartar Singh*, *Horace B. Dunnicliff*.

Khan, Ghulam Safdar, Veterinary College, Lahore. Lecturer in Chemistry, Veterinary College, Lahore. Passed B.Sc. examination in 1920 from Punjab University. Appearing in the M.Sc. examination 1922. Special work: (1) Separation of different qualities of turpentine oil. (2) Solubility of sulphur dioxide in sulphuric acid of different concentration at constant temperature. (*Signed by*) S. R. Khosla, N. A. Yajnik, E. T. Dean.

Lassen, Svend Hald, "Briarwood," Manorgate Rd., Kingston-on-Thames. Danish. Works Manager. Graduated at the University of Copenhagen. Assistant lecturer at the Royal Mineralogical Museum, Copenhagen, 1913–14. Participated in an Arctic expedition to North Greenland as mineralogist. At

present works manager to Water Softeners, Ltd. (synthetic aluminium silicates and dyestuffs). (*Signed by*) Harald Faber, Bernard Dyer, Robt. G. Grimwood.

LLOYD, WILLIAM DAWSON, 42, Tavistock Road, Westbourne Park, W.11. Medical, Veterinary, and Pharmaceutical Representative. Fifteen years' analytical and pharmaceutical experience—manufacture of bismuth salts, urine analysis, etc. (*Signed by*) A. E. Mills, Geo. A. Pemberton Wright, Herbert A. Mills.

LYNCH, PHILIP PATRICK, Church Street, Timaru, N.Z. Medical Student. B.Sc. (N.Z.). First and second professional examinations for degrees M.B., Ch.B. (N.Z.). 1918 Asst. Chemist, Department of Agriculture, Wellington. At present assistant to C. S. Hicks, M.Sc., A.I.C., Public Analyst, Dunedin (Fellow). Engaged in biochemical research on goitre, nephritis, and diabetes under Professor of Pathology at University of Otago and in collaboration with C. S. Hicks, M.Sc. (Fellow). (*Signed by*) C. S. Hicks, Thomas H. Easterfield, Fredk. P. Worley, J. K. H. Inglis.

MACALPINE, FRANCIS GEOFFREY, Broad Oak, Accrington, Lancs. British. Managing Director of Coal-Tar Distillation and Ammonia Works. Degree of B.Sc. of Manchester University. Twelve months' study of coal carbonisation and working up of by-products at Birchenwood Collieries, Kidsgrove. I desire to join the Chemical Society so as to be kept informed of the progress of chemistry through the Transactions of the Society and its Library. (*Signed by*) B. Prentice, E. Clark, D. V. Hollingworth.

MCDOWALL, FREDERICK HENRY, Knox College, Dunedin. Research Student, Otago University. M.Sc. with 1st Class Honours. Thesis on "Constitution and Synthesis of Menthol." Smeaton Research Scholar of Otago University, 1921–22. Student demonstrator and half-time assistant to Dr. Inglis in Chemistry Department, Otago University, 1919, 1921–22. (*Signed by*) J. K. H. Inglis, C. L. Carter, C. S. Hicks.

MCKENZIE, KENNETH, "Endrick," Hamilton Rd., Cambuslang. Scotch Analytical Chemist. For the past ten years engaged in the study and practice of analytical chemistry. Training: at Royal Technical College, Glasgow, and with Messrs. R. R. Tatlock & Thomson, Public Analysts, Glasgow. At present assistant chemist with Lantaro Nitrate Co., Ltd., Chile, with complete control of all analytical work. Desirous of joining Chemical Society for purpose of keeping in touch with advances in analytical chemistry. Originator of method for determination of perchlorates in small quantities in caliche, etc. Refinement of ferrous sulphate assay for nitrate in caliche, whereby experimental error is reduced from $\pm 4\%$ to $\pm 0{\cdot}6\%$. (*Signed by*) R. T. Thomson, A. R. Campbell, George Grant, Alex. W. McLaren.

MCNICOL, REGINALD ARTHUR, "Birnam," Rotherfield Road, Carshalton, Surrey. British. Bio-chemist to the Jersey Tomato and Fruit Preserves, Ltd., St. Heliers, Jersey (J. Lyons & Co.). Pupil Sutton (Surrey) County Secondary School, Sept. 1912–July 1916. Student Battersea Polytechnic Sept. 1916–June 1922. B.Sc. Lond. (3rd Class Hons. in Chemistry), Oct 1920. M.Sc. Lond., May 1922. Thesis: "The Preparation and Optical Properties of the Aliphatic Ethers of Secondary Octyl Alcohol." (*Signed by*) Leslie Hall, J. Kenyon, Harold Hunter, J. L. White.

MALKIN, THOMAS, Golden Square, Warrington. British. Research Student in Chemistry, Victoria University, Manchester (Ph.D. candidate). B.Sc. (London), Hons. Chemistry. A.I.C. Two years' post-graduate research at College of Technology, Manchester. Part-time lecturer in chemistry at Warrington Technical Institute, 1920–22. (*Signed by*) Arthur Lapworth, Frank Lee Pyman, Leslie Randal Ridgway.

MARTIN, ARCHIBALD ROY HAMMOND, 8, Kingsland Rd., Worthing, Sussex. British. Student. At St. John's College, Cambridge, read for Nat. Sci. Tripos, Part I, for 2 years, taking the B.A. degree in June, 1921. Read for Nat. Sci. Tripos, Part II, in chemistry for 1 year, passing in Class 2. (*Signed by*) W. G. Palmer, T. M. Lowry, Charles T. Heycock.

MATTHEWS, JOSEPH KEITH, M.A. (Cambridge), Cedric House, Rainhill, Lancashire. British. Fuel Technologist (Messrs. Pearson & Knowles Coal & Iron Co., Warrington, Lancs.). 1908, 1st Class Honours in Natural Sciences Tripos, Camb. (including chemistry). 1909, 2nd Class Honours in Part II Chemistry Tripos, Camb. From 1909 the applicant has been in a responsible position in chemical industry, first with Messrs. Pilkington Bros. and later with the above-named firm. (*Signed by*) A. J. Berry, Charles T. Heycock, S. R. Adcock, W. E. S Turner.

MOORHEAD, CHARLES WILLIAM, 23, Newbridge Rd., Bath. Chemist to Meldon Valleys Co., Ltd. Twenty-five years' experience in drug and chemical trades, glass technology, manufacturing chemistry. (*Signed by*) Alan E. Gardiner, Alfred Mander, A. E. Mills.

MOSS, JOHN EWART, 298, Franklin Road, Kings Norton, Birmingham. Research Student. B.Sc. (1st Class Honours in Chemistry) and M.Sc. (Birm.). (*Signed by*) G. T. Morgan, S. R. Carter, Wm. Wardlaw, E. Ashley Cooper, C. J. V. Bews, J. D. Main Smith.

NATH, DINA, Jullundhur City (Punjab), India. At present assistant chemist to Bhatni Sugar Works, Gorakhpur (District), United Provinces, India. Graduate in Science of the Punjab University. Specialist in soap manufacture. Written a paper on soapmaking with special reference to Indian conditions. At present working on "The Action of Alkalies on Rosine under Different Conditions." Certificate from the Professor-in-Charge with regard to the ability in applied chemistry is attached herewith. (*Signed by*) Bhagwan Das Batta, N. A. Yajnik, E. T. Dean.

NIELSEN, TORKILD HAASTRUP, Knockhall Lodge, Greenhithe, Kent. Danish. Chemist at Kent Cement Works of the Associated Portland Cement Manufacturers, Limited. Bachelor of Science in chemical engineering from the Royal Technical College in Copenhagen. (*Signed by*) H. Baggesgaard Rasmussen, Chr. Winther, J. J. Fox, S. P. L. Sörensen.

NISHIKAWA, HIDEJIRO, 3, Hachimancho, Asakusa, Tokyo, Japan. Japanese Government Research Scholar. Graduate of the section of agricultural chemistry of the Agricultural Department of the Imperial University of Tokyo, Japan. Research student of the Chemistry Department, St. Andrews University. (*Signed by*) Robert Robinson, J. C. Irvine, John Pryde, E. L. Hirst.

NOMURA, HIROSHI, Chemical Institute, Imperial University, Sendai, Japan. Japanese. Assistant Professor of Chemistry. Graduated at the Tokio Imperial University of Japan, engaged in research for one and a half years under Professor W. H. Perkin. Assistant Professor of Chemistry, Tohoku University, since 1914. (*Signed by*) W. H. Perkin, E. Hope, S. G. P. Plant, E. N. Allott, W. Davies, A. F. Titley, Thos. H. Durrans.

PAGE, ALBERT BRAMAH PEARCE, 27, Tanza Road, Hampstead, N.W.3. Research Student. Associate Royal College of Science. I desire to keep in touch with chemical progress through the *Journal* of the Society. (*Signed by*) James C. Philip, H. J. T. Ellingham, Olive Workman.

PICKLES, HAROLD, Gasworks, Kildwick, nr. Keighley. Chemist and Assistant Engineer, Keighley Corporation Gasworks. Studied chemistry (theoretical, practical, and industrial) at Keighley Trade and Grammar

School, Halifax Technical College, and Leeds University. Nine years' laboratory experience as gasworks chemist. Contributed papers to the *Gas World* on the properties of gaseous mixtures. (*Signed by*) H. Harper, Wm. Cranfield, John Wilkinson.

Pooley, Joseph Edwards, 1, Margaretting Road, Manor Park, E.12. British. Principal, "Sandringham" Central School, Forest Gate, E.7. Trained Certificated Teacher. Inter. B.Sc. (London), chemistry as a subject. Inter. B.Sc. (Econ.), London. L.C.P. (chemistry as a subject). B. of E. Certs. in P. and T. Chemistry, advanced stage. Science lecturer at Woolmore St. L.C.C. Evening Institute, Sessions 1914–18. (*Signed by*) Evan D. Griffiths, Léon E. Walling, Alfred W. J. Denney.

Potts, Thomas Trevor, 60, Christ Church Square, Macclesfield. British. Chemist to Messrs. Robert Fletcher & Son, Ltd., Kearsley Paper Works, Stoneclough, and Greenfield Paper Mill, Greenfield, Yorks Educated at Macclesfield Grammar School (science student under Fisher Advanced Courses Scheme). Matriculated 1917. Part-time student, Manchester Municipal College of Technology in Chemistry and Technology of Paper Manufacture. Held above post from August 1919, since when I have been engaged in general chemical control of processes and private research work in chemistry as applied to the manufacture of high-grade tissues, including original work on new processes of manufacture and methods of analysis. (*Signed by*) William Bacon, Alfred Holt, Julius Hübner.

Pound, James Robert, 601a, Dana St., Ballarat, Victoria, Australia. Lecturer in Chemistry, the School of Mines, Ballarat. M.Sc. (Melb., Chemistry). Author of papers on Ether and Sulphuric Acid, Trans., 1911 and 1922, and on Treatment of Wolfram Ores, *Proc. Australian Inst. Min. Met.*, 1919. Formerly research chemist at Amalgamated Zinc (De Bovay's), Ltd., Broken Hill, N.S.W., and superintendent of Magnetic Separation Works, S. & M. Syndicate, Ltd., Launceston, Tas. (*Signed by*) Orme Masson, A. C. D. Rivett, D. Avery.

Prasad, Nagendra, Ranchi, Behar and Orissa, India. Deputy Collector. B.Sc. with Honours in Chemistry. M.Sc. with Thesis and Organic Chemistry as the special subject. Joint author of "Iodination by means of Nitrogen Iodide or by means of Iodine in presence of Ammonia," published in the *Journal of the American Chemical Society*, Vol. XXXIX, 1917. Worked as a research student for some time at the Agricultural Research Institute at Pusa; has a private laboratory of his own; wants to be in touch with current literature on chemistry. (*Signed by*) Phuldeo Sahay Varma, A. S. Khan, Chandra Bhushan Roy, R. L. Datta.

Prideaux, Edmund Brydges Rudhall, 6, Arboretum Street, Nottingham. British. M.A. and B.Sc. (N.Z.), D.Sc. (Lond.), F.I.C. Lecturer in Chemistry and Research Chemist at University College, Nottingham. Research falls mainly under the following heads: The compounds of fluorine; the atomic and molecular volumes of liquid elements and their liquid compounds; electrochemical investigations of solutions by the conductivity and electromotive force methods, with special reference to acidity and alkalinity; electrolytic corrosion; the evaporation and deliquescence of salt solutions; the chemical factors controlling the alkalinity of sea water. My books deal with the arithmetical problems of physical chemistry and with the theory and control of acidity and alkalinity, with special reference to the use of indicators. (*Signed by*) F. Stanley Kipping, F. G. Donnan, A. J. Allmand.

Pullen, Alfred Norman Douglas, The Larches, Greenham Common,

Newbury. English. Late Analyst to China Mining and Metal Co., Ltd., Hong Kong. In charge of smelting and refining works to above Co., 1918–22. Pharmacist to Hong Kong Government, 1914–17, and assistant analyst, 1915–16. Assistant to T. Tickle, B.Sc., F.I.C., Boro' Analyst, Exeter, 1912–13. Major Diploma, Pharmaceutical Society and silver medallist (chem.). 1912. Paper on "Iodine Ointment," *Pharm. Journ., Nov. 16th, 1912*. (*Signed by*) A. W. Crossley, Thomas Tickle, Frank Comyns.

RILEY, GEORGE CLIFFORD, B.A., B.Sc., 15, Wellington Square, Oxford. British. Research Chemist. Works chemist on production of explosives, 1915–19. Student at Oxford University, 1914–15 and 1919–21, taking 2nd Class Honours, Final Honours Chemistry School, and B.A. 1920. One year's research work in organic chemistry and B.Sc. degree, 1921. Research assistant to Professor W. H. Perkin, M.A., F.R.S., 1921 to present date. Publication: "The Chlorination of Benzoyl Chloride" (with Edward Hope), accepted for publication in the *Journal* of the Society. (*Signed by*) W. H. Perkin, N. V. Sidgwick, E. Hope, W. Davies, A. F. Titley, D. Ll. Hammick, S. G. P. Plant.

ROBERTSON, THOMAS ABRAHAM, "Sassafras," Rickard Road, Bankstown, N.S.W. Chemist and Manager, Austral Starch Co., Nelligen, N.S.W. Student at Sydney Technical College in Inorganic Chem. complete course, Theory and Practical. Organic Chemistry 3 years, 1907–13. Matriculated for Sydney University, 1914. Assist. in Physiological Research Lab., Sydney University, for 2 years, 1910–12. Member of Sydney Technical College Chemical Society for 8 years. Special representative of commercial firms for 2 years. At present Organic Chemist and Manager of Austral Starch Co., Nelligen, N.S.W. Paper and exhibits before Sydney Tech. Coll. Chem. Society: "Chemical Substances in Human Body" and "Glandular Secretion of Iodine in Blood Stream;" other papers in course of preparation. (*Signed by*) Richard W. Challinor, Arthur R. Penfold, Archibald D. Ollé, Robt. Grant, George Z. Du Pain.

RUSHWORTH, BURKE, 4, West Park Terrace, Healey, Batley, Yorks. English. Manager, Chemist Department, Batley Co-operative Society, Ltd. Certificate winner Army Science College, Bonn University, Germany, having studied there after the armistice. Ex-student S.W. Polytechnic Institute, Chelsea, having taken the Minor Pharmaceutical Exam. Now working for the Major and F.S.M.C. diplomas. (*Signed by*) C. Morton, F. H. Lowe, F. Arnall.

SCHOLEFIELD, ARTHUR, Poulton Hey, Bromborough, Cheshire. British. Director of Powell & Scholefield, Ltd., Chemical Manufacturers, Edge Hill, Liverpool. Interested in the chemical industry, and desirous of keeping in touch with scientific research. (*Signed by*) Harold Rogerson, E. C. C. Baly, I. M. Heilbron.

SINGH, GOPAL, "The Brij," Gawalmandi, Lahore, India. Indian. Professor of Chemistry, Dyal Singh College, Lahore. B.Sc. with Honours in Chemistry, M.Sc. 1st Class First. For some time research student of the Punjab University. For about 2½ years Professor of Chemistry at the Dyal Singh College, Lahore. Joint author of the paper (*J.C.S.*, T., 1920, p. 980). Author of the paper (*J.C.S.*, T., 1922, May, p. 782) "Phototropy of Inorganic Salts, Cuprous Chloride, and Bromide." (*Signed by*) N. A. Yajnik, Horace B. Dunnicliff, Tara Singh Mahal.

SMITH, GEORGE VICTOR, Westleigh, Eggington Rd., Wollaston, Stourbridge. British. Student. A.R.C.S. (Chemistry). Formerly Assistant Master, King Edward VI. Grammar School, Stourbridge. (*Signed by*) James C. Philip, M. A. Whiteley, H. F. Harwood, J. N. Sugden, J. G. Howarth.

SNEDKER, STANLEY JAMES CORRALL, "The Rowans," Wood Hey, Rock

Ferry, Cheshire. Senior Assistant, Department of Organic Chemistry, University of Liverpool. Carrying out original research. I wish to keep in touch with current chemical literature. *(Signed by)* E. C. C. Baly, I. M. Heilbron, Harold Rogerson, J. S. Buck.

SNOW, OSCAR WALTER, Graeme's Bank, Hatch End, Middlesex. British. Research Student. B.A. (Oxon.) [Part I, Final Honours School of Chemistry]. Scholar of New College, Oxford. At present engaged in research for Part II. *(Signed by)* W. H. Perkin, S. G. P. Plant, N. V. Sidgwick, Allan F. Walden, E. Hope.

STOYLE, FRANCIS WILBERT, 37, Kansas Avenue, Belfast. British. Student. B.Sc. (1st Class Hons.), Queen's University, Belfast, 1921. M.Sc. Queen's University, Belfast, 1922. *(Signed by)* Robert Robertson, A. W. Stewart, H. Graham.

THEOBALD, LESLIE STUART, 3, Ennismore Avenue, Chiswick, W.4. Student. A.R.C.S. course in chemistry just completed. *(Signed by)* James C. Philip, H. F. Harwood, J. N. Sugden.

THOMPSON, WILLIAM, "Ravensworth," Cockton Hill, Bishop Auckland. Student. Bachelor of Science, University of Durham. Degree obtained June 1922. *(Signed by)* P. Phillips Bedson, W. N. Haworth, Grace C. Leitch.

TIMMIS, LAURENCE BARNETT, 19, Trinity Marsh Lane, Waltham Cross, Herts. British. Chemist. M.Sc.Tech. (Manchester), A.I.C. Employed at Messrs. Allen & Hanbury's, London, as assistant chemist in the analytical and research departments. *(Signed by)* F. W. Gamble, Frank Lee Pyman, John K. Wood.

TRUSZKOWSKI, RICHARD, Koszykowa 21, m. 3, Warsaw, Poland. British. Research Student. B.Sc. *(Signed by)* Stanley A. Mumford, O. L. Brady, E. H. Thierry.

VINEY, HUMPHREY TERENCE, *Bramerton, Blakebrook, Kidderminster.* British. Carpet Industry, Application of Chemical Science to. Honours B.Sc., Birmingham University. *(Signed by)* G. T. Morgan, S. R. Carter, E. A. Cooper, C. E. Wood.

WALL, THOMAS JOHN, Northcote, Alexandra Road, Malvern. British. Research Student. Took Part I of Final Honour School of Natural Science at Oxford in June last and am now doing research in Organic Chemistry for Part II. Exhibitioner of Christ Church, Oxford. *(Signed by)* S. G. P. Plant, N. V. Sidgwick, E. Hope.

WARD, HARRY, *Toynbee Hall, 28, Commercial St., E.1.* British. Research Chemist. B.Sc. (Hons.) (Leeds), M.Sc., A.I.C. 2½ years' experience as research chemist with the General Electric Company. *(Signed by)* R. Le Rossignol, L. D. Goldsmith, William Singleton.

WATSON, STEPHEN JOHN, School of Agriculture, Reaseheath Hall, Nantwich, Cheshire. British. Demonstrator in Agricultural Chemistry, Armstrong College (in the University of Durham). Degree of B.Sc. in agriculture, Armstrong College, Durham University. Registered student of the Institute of Chemistry. Research on potash. Paper accepted for publication by the Society of Public Analysts. Eighteen months' experience in coal analysis. Delivered 50 lectures to Elementary Class in Agricultural Chemistry. *(Signed by)* S. Hoare Collins, Philip Buckle, Lionel Orange, Harold Scragg.

WILLIAMS, ALEXANDER MITCHELL, Shirley Institute, Didsbury, Manchester. British. Research Chemist. M.A., D.Sc. Author or joint author of over a dozen scientific papers on physical chemistry (including T., 1920, **117**, p. 844). *(Signed by)* Arthur W. Crossley, D. Clibbens, R. G. Fargher, J. C. Withers.

WOODWARD, ERIC RICHARD BORAMAN, The Vicarage, Herne Bay, Kent. Chemist. Graduate (B.Sc. in Chemistry and Physics) of the University, Liverpool. (*Signed by*) I. M. Heilbron, E. C. C. Baly, Herbert H. Froysell.

WOOLCOCK, WILLIAM JAMES UGLOW, C.B.E., M.P., 166, Piccadilly, W.1. British. General Manager, Association of British Chemical Manufacturers. Pharmaceutical Chemist. Barrister-at-law. (*Signed by*) M. O. Forster, N. Garrod Thomas, E. V. Evans, E. F. Armstrong.

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The following Certificate has been authorised by the Council for presentation to ballot under Bye-law I (2):

GOVILA, BABU LALL, Gwalior. Hindu. Principal of Central Polytechnic Institute, and Director of Industrial and Technical Education, Gwalior State. (1) Studied chemistry in Indian University College and Japan. (2) Graduated in Tokyo (Japan) in colour chemistry. (3) Studied weaving and spinning in Japan. (4) Worked as Professor and Demonstrator of applied chemistry. (5) Worked in dyeing, calico printing, and soap works in Japan and India. (6) Worked as Principal of the Institute of Textile Technology, Chanderi. (7) Worked in colour research and coal-tar products. (8) Working as Principal of Central Polytechnic Inst. with a department for applied chemistry, and training students in dyeing, calico printing, soap-making, coal-tar distillation, intermediate products, and coal-tar dyes, for the City and Guilds of London Examinations, for the last four years. (*Signed by*) Puran Singh.

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## ADDITIONS TO THE LIBRARY.

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AGRICULTURAL LEDGER. Calcutta 1892—1912. (*Reference.*)

CHEMICAL ENGINEERING AND THE WORKS CHEMIST. Vols. I—V. Dover 1911—1915. (*Reference.*)

DINGLERS POLYTECHNISCHES JOURNAL. Vols. CCIX—CCLVI. Stuttgart 1876—1885. (*For Circulation.*) [Wanting Vol. CCXXXV.]

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FUEL IN SCIENCE AND PRACTICE. A journal of the scientific and economic use of fuels. (Being the Record of the Coal Researc Club.) Vol. I, etc. London 1922+. ill. (*Reference.*) [Monthl supplement to The Colliery Guardian.]

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Revision of Methods. 2nd edition, revised to November 1, 1919. Washington, D.C. 1921. pp. xii+418. ill. (*Recd.* 21/8/22.)

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—— Vorlesungen über die Geschichte der Chemie. Leipzig 1922. pp. viii+468. (*Recd.* 10/10/22.)

ROBERTSON, GEORGE SCOTT. Basic slags and rock phosphates. Cambridge 1922. pp. xvi+120. ill. 14*s.* net. (*Recd.* 20/6/22.)

ROBINSON, CLARK SHOVE. The elements of fractional distillation. New York 1922. pp. x+206. ill. 12*s.* 6*d.* net. (*Recd.* 21/6/22.)

ROGERS, ALLEN. Practical tanning: a handbook of moderr practice and processes as applied in the manufacture of leather anc allied products. London 1922. pp. xxvi+700. ill. 45*s.* net (*Recd.* 6/7/22.)

RYDBERG, JOHANNES ROBERT. Untersuchungen über die Beschaf fenheit der Emissionsspektren der chemischen Elemente. Trans lated from the French by A. VON OETTINGEN. Edited by MANN SIEGBAHN and A. VON OETTINGEN. (Ostwald's *Klassiker*, N 196.) Leipzig 1922. pp. xvi+214. ill. (*Recd.* 14/9/22.)

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## IV. *Pamphlets.*

AIR MINISTRY. *Meteorological Office.* Advisory Committee Atmospheric Pollution. Report on observations in the y ending March 31st, 1921. Forming the seventh report of Committee for the Investigation of Atmospheric Pollution. Lon 1922. pp. 31. ill.

ALBERTA. *Scientific and Research Council.* Second ann report. Edmonton 1922. pp. 86. ill.

AMERICAN INSTITUTE OF BAKING. Bulletin No. 8. The diast enzymes of wheat flour and their relation to flour strength. LOUYS A. RUMSEY. 1922. pp. 86. ill.

—— Bulletin No. 9. Flour strength as influenced by addition of diastatic ferments. By FERDINAND A. COLLATZ. 1 pp. 74. ill.

BELAIEW, NICHOLAS TIMOTHY. Heat treatment of steel. (F the *Russian Economist*, 1922, 2.)

—— Henry Marion Howe (1848—1922). (From the *Ru Economist*, 1922, 2.) ill.

# PROCEEDINGS

OF THE

# CHEMICAL SOCIETY.

*Ordinary Scientific Meeting*, Thursday, December 7th, 1922, at 8 p.m., Professor SAMUEL SMILES, O.B.E., D.Sc., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of:

| | Elected. | Died. |
|---|---|---|
| Thomas William Dukes ................. | Dec. 5th, 1889. | Nov. 8th, 1921. |
| David Thomas Williams ................. | Feb. 20th, 1908. | Jan. 29th, 1922. |

Mr. G. F. Underhay was formally admitted a Fellow of the Chemical Society.

*Certificates were read for the first time in favour of:*

Arthur John Attwood, A.R.C.S., 11, Frederick Crescent, S.W. 9.
Frederick Bradshaw, M.A., D.Sc., 78, Rothbury Terrace, Heaton, Newcastle-on-Tyne.
Charles Crossley Mann Broughton, B.Sc., 2, Upton Road, Bexleyheath.
John Southwell Bousfield, A.R.C.S., 2, Lyndale, Childs Hill, N.W. 2.
Leslie John Couzens, 101, Kensington Avenue, Manor Park, E. 12.
Ernest Cecil Craven, 59, Southern Road, Plaistow, E. 13.
James Cooper Duff, M.Sc., F.I.C., 13, Queen's Road, Erdington, Birmingham.
John Kenneth Giles, B.Sc., Hillcrest, Arkley, Barnet.
John Preedy Griffiths, B.Sc., A.R.C.S., 15, Hazelwood Lane, Palmer's Green, N. 13.
Leslie Julius Harris, B.Sc., 18, The Park, Ealing, W. 5.
John Laker, B.Sc., 8, Allerton Road, N. 16.
George Arnold Medley, 45, Hill Top Road, Dalton, Huddersfield.
William James Osborn, 12, West Square, Southwark, S.E. 1.
Francis James Paxon, B.Sc., A.R.C.S., 30, St. George's Road, Palmer's Green, N.13.
Edwin William Stanley Press, 4, Porchester Square, Hyde Park, W. 2.
Edward Ebenezer Price, The Haven, Dormans Park, East Grinstead.
Edgar Sanders, The White House, Blackwell, Worcestershire.
Hedley Archibald Sloman, B.A., A.I.C., Robinhood, Undercliff Gardens, Leigh-on-Sea, Essex.
Arthur Roy Stark, 76, De la Pole Avenue, Hull.
Frederick Vincent Tideswell, M.Sc., Dept. of Fuel Technology, The University, Sheffield.

Frederic Jenner Tritton, B.Sc., 1F, Vicarage Mansions, West Green, N. 15.
Paulo Laure Vanderstichele, M.Sc., Bedford College for Women, Regent's Park, N.W. 1.
Stanley Douglas Weaver, B.Sc., A.R.C.S., 27, Hastings Road, Maidstone.
Harold Wood, B.Sc., 39, Edmund Street, Seedley, Manchester.

The CHAIRMAN announced that a circular had been sent out to Fellows with regard to the new weekly Journal entitled "Chemistry and Industry," and that the Journal for 1923 would be supplied to Fellows for the sum of 10*s*.

Mr. C. S. Grace and Dr. G. A. R. Kon were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Robert Allanson.
Thomas Cuthbert Allchin.
James Wilson Armit, M.A.
Leopold Louis Bacarese.
Leslie Bains, B.A., B.Sc., A.I.C.
Menghraj Choithram Batbija, B.A.
Nicholas Timothy Belaiew, C.B.
James Bell.
Donald Charles Broome.
Walter Ferguson Buist, B.Sc.
Stanley Robert Bult.
Arthur Josiah Burford.
George Joseph Burrows, B.Sc.
William Leslie Carter.
Sydney George Cavigan.
John Hardwick Long Champion, B.Sc.
Katragadda Seshachalam Choudary, M.A., M.Sc.
Elliot Martin Christie, M.Sc.
Frederick Stanley Clarke.
Allin Cottrell.
John Arnold Cranston, D.Sc.
Hugh John Curnow.
Edward Dance, B.Sc.
Wilfred Thomas Grey Davies, B.Sc.
Milton Dewhurst, B.Sc., A.I.C.
Richard Victor Eaton, B.Sc., A.R.C.S.
Norman Evers, B.Sc., F.I.C.
Joshua William Farmery, M.A., A.I.C.
Samuel Frederick Ford.
Roy Gardner, B.Sc.
Philip Henry Gifford, B.Sc.
Babu Lall Govila.
Roland Hall Griffith, B.A.
Reginald William Griffiths, B.Sc.
John Masson Gulland, B.Sc.
Herbert Haigh, B.Sc.
Lucy Higginbotham, M.Sc.
Thomas Edward Hubbard.
James Ernest Humphries, B.A., M.Sc.
John Huntley.
Sydney Alfred Hurren, M.C.
Habib Iskander.
John Watson Jenkin, B.Sc., A.I.C.
John Ernest Jewell.
Edgar Jones.
Jan Kalff, D.Chem.
Shankar Nath Kapur, B.Sc.
Ghulam Safdar Khan, B.Sc.
Svend Hald Lassen.
William Dawson Lloyd.
Philip Patrick Lynch, B.Sc.
Francis Geoffrey Macalpine, B.Sc.
Frederick Henry McDowall, M.Sc.
Kenneth McKenzie.
Reginald Arthur McNicol, M.Sc.
Thomas Malkin, B.Sc., A.I.C.
Archibald Roy Hammond Martin, B.A.
Joseph Keith Matthews, M.A.
Charles William Moorhead.
John Ewart Moss, M.Sc.
Dina Nath.
Torkild Haastrup Nielsen, B.Sc.
Hidejiro Nishikawa.
Hiroshi Nomura.
Albert Bramah Pearce Page, A.R.C.S.
Harold Pickles.
Joseph Edwards Pooley.
Thomas Trevor Potts.
James Robert Pound, M.Sc.
Nagendra Prasad, M.Sc.
Edmund Brydges Rudhall Prideaux, M.A., D.Sc., F.I.C.

Alfred Norman Douglas Pullen.
George Clifford Riley, B.A., B.Sc.
Thomas Abraham Robertson.
Burke Rushworth.
Arthur Scholefield.
Gopal Singh, M.Sc.
George Victor Smith, A.R.C.S.
Stanley James Corrall Snedker.
Oscar Walter Snow, B.A.
Francis Wilbert Stoyle, M.Sc.
Leslie Stuart Theobald, A.R.C.S.
William Thompson, B.Sc.
Laurence Barnett Timmis, M.Sc.Tech., A.I.C.
Richard Truszkowski, B.Sc.
Humphrey Terence Viney, B.Sc.
Thomas John Wall, B.A.
Harry Ward, M.Sc., A.I.C.
Stephen John Watson, B.Sc.
Alexander Mitchell Williams, M.A., D.Sc.
Eric Richard Boraman Woodward, B.Sc.
William James Uglow Woolcock, C.B.E.

The following papers were read:

"The isoelectric condition of gelatin." By S. O. Rawling and W. Clark.

"Studies on metal hydrides. The electrolytic formation of stibine in sulphuric acid and caustic soda solution." By H. J. S. Sand, E. J. Weeks, and S. W. Worrell.

"Three carbon tautomerism in the *cyclo*propane series." By F. R. Goss, C. K. Ingold, and J. F. Thorpe.

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Meeting held in the Lecture Hall of the Institution of Mechanical Engineers, on *Thursday, December 14th, 1922, at 8 p.m., Professor* H. B. Dixon, C.B.E., M.A., F.R.S., Vice-President, in the Chair.

Professor C. H. Desch, D.Sc., *Ph.D., delivered his Lecture* entitled: "The metallurgical applications of physical chemistry." A vote of thanks to the Lecturer, proposed by Professor T. M. Lowry and seconded by Dr. N. V. Sidgwick, was carried with acclamation, acknowledgment being made by Professor Desch.

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Ordinary Scientific Meeting, Thursday, December 21st, 1922, at 8 p.m., Sir James Walker, D.Sc., *F.R.S., President, in the Chair.*

The President referred to *the loss sustained* by the Society, through death, of:

| | Elected. | Died. |
|---|---|---|
| Henry Ruchot Fairweather ........................ | Dec. 4th, 1910. | Sept. 11th. |

Messrs. Duncan P. Woosley and Donald C. Broome were form admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

George James Alexander, B.Sc., 1, Terrace Road, Upton Manor, E. 13.
Harold Eugene Buckley, M.Sc., 273, Wigan Road, Bolton.
Robert Kenneth Callow, B.A., B.Sc., 17, Sutherland Street, S.W. 1.
Alexander Coutie, 4, Priestfield Road, Edinburgh.

Thomas Arthur Harrison, 64, Eastwood Road, Goodmayes.
Herbert Frederick Miller, B.Sc., A.I.C., Griffith John College, Hankow China.
William Owen Murch, B.Sc., National Institute for Medical Research, Hampstead, N.W. 3.
James Herbert Oliver, B.Sc., 22, Avenue Gardens, Acton, W. 3.
Thomas Workman Orr, A.I.C., Antofagasta, Chile.
Edward Arthur Perren, 70, Denton Road, N. 8.
Frank Victor Raleigh, B.A., B.Sc., 6, Cavendish Road, Harringay, N. 4.
Helena Charlotte Randall, B.Sc., A.R.C.S., 57, Farnham Road, Guildford.
Jerry Robertson, 38, Church Street, Heckmondwike.
*Douglas Rosebery Snellgrove, B.Sc., 73, Millbrook Road, Southampton.*
Montague Williams, B.Sc., Cleveland Cottage, The Grove, Isleworth.

Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of :

Donald Hatch Andrews, B.A., Stirling Chemical Laboratory, New Haven Conn., U.S.A.
Arthur D. Little, Charles River Road, Cambridge, Mass., U.S.A.

The following papers were read :

"Benzbisthiazoles. Part II." By S. R. H. EDGE.

"Ring-chain tautomerism. Part IV. The effect of the methyl ethyl grouping on the carbon tetrahedral angle." By B. SINGH and J. F. THORPE.

## ORDINARY SCIENTIFIC MEETING.

The next Ordinary Scientific Meeting will be held on Thursday, January 18th, 1923, at 8 p.m.

## BUREAU FOR PHYSICO-CHEMICAL STANDARDS.

Under the auspices of the Union Internationale de la Chimie Pure et Appliqué, a "Bureau des Étalons Physico-chimiques" has been established at Brussels (Université, rue des Sols). This is intended as a centre for the preparation and collection of substances of the highest purity, the physical constants of which have been determined with the utmost possible precision, and which shall be at the disposal of research workers. An appeal is accordingly made to chemists generally to collaborate in the provision of highly purified products from which the standards may be prepared.

It is further proposed to collect the scattered literature dealing with the preparation of substances in a condition of the highest purity, and with the determination of their physical constants. With this object in view, investigators are invited to furnish the Bureau with copies of any relevant papers.

List of Papers received between November 17th, 1922, and December 21st, 1922:

"Negative hydrogen and the electronic formula of benzene." By H. S. Fry.

"Elimination of the amino-group of tertiary amino-alcohols. Part I." By A. McKenzie and A. C. Richardson.

"Studies on metal hydrides. The electrolytic formation of stibine in sulphuric acid and caustic soda solution." By H. J. S. Sand, E. J. Weeks, and S. W. Worrell.

"Some derivatives of methylene-diquinalide and their relationship to the carbocyanines." By F. M. Hamer.

"Dyestuffs derived from heterocyclic bases containing reactive methyl groups." By J. L. B. Smith.

"1 : 8-*bis*-Naphthylene-indigo." By S. Dutt.

"Dyes derived from diphenic anhydride." By S. Dutt.

"The effect of metallic oxides and metals on the oxidation of vegetable oils in presence of fibrous material. Part I. The rise in temperature and the changes in iodine value." By M. B. Rāne, P. N. Roy, and L. Gupta.

"Synthesis of substituted thianthrens. Part I. Thianthren and nitrothianthren." By S. Krishna.

"The absorption of moisture by coal (and other fuels). Part I. A relation between degree of humidity in the air and moisture content of coal." By B. Moore and F. S. Sinnatt.

"The nitration of benzaldehyde." By O. L. Brady and S. Harris.

"The investigation of *meso*-thioanthracene derivatives. Part I. Observations on the production of dithioanthraquinone, dithiodianthrone, and other closely related derivatives." By I. M. Heilbron and J. S. Heaton.

"The chemistry of the glutaconic acids. Part XIII. The isomerism due to retarded mobility." By J. F. Thorpe and A. S. Wood.

"The chemistry of the glutaconic acids. Part XIV. Three carbon tautomerism in the *cyclo*propane series." By F. R. Goss, C. K. Ingold, and J. F. Thorpe.

"The quantitative absorption of light by simple inorganic salts. Part II. The chlorides of arsenic, antimony, and bismuth." By A. K. Macbeth and N. I. Maxwell.

"The production and reactions of 2-dithiobenzoyl." By M. McKibben and E. W. McClelland.

"The influence of papaverine on the optical activity of narcotine in acid solution." By H. E. Annett.

"The higher oxide of cobalt." By O. R. Howell.

"The calculation of the colour of monocyclic substances by assigning an absorption band to each possible tautomeric formula of the substance." By J. Moir.

"The application of the Hoesch reaction to the preparation of some dihydroxy- and trihydroxy-deoxybenzoins." By E. Chapman and H. Stephen.

"Studies on thallium compounds. Part II. The reduction of thallic compounds with ferrous sulphate and with sodium arsenite." By A. J. Berry.

"The constitution of the disaccharides. Part VII. Sucrose." By W. N. Haworth and W. H. Linnell.

"The determination of the dissociation pressures of hydrated salts by a dynamical method. Part II." By J. R. Partington and D. B. Huntingford.

"The constitution of the disaccharides. Part VIII. Sucrose." By W. N. Haworth and J. G. Mitchell.

"Benzbisthiazoles. Part II." By S. R. H. Edge.

"The upper limit of diazotisability in the benzene series. Diazo-derivatives of mesitylene." By G. T. Morgan and G. R. Davies.

"Researches on residual affinity and co-ordination. Part XV. Interactions of acetylpropionylmethane and the tetrachlorides of selenium and tellurium." By G. T. Morgan and H. G. Reeves.

"Studies in the normal butyl series. Part II. The four stereo-isomeric β-γ-di-*p*-tolylamino-*n*-butanes." By G. T. Morgan and W. J. Hickinbottom.

"The formation and stability of spiro-compounds. Part X. *Spiro*-compounds derived from *cyclo*heptane." By J. W. Baker and C. K. Ingold.

"The sorption by carbon prepared from pure organic compounds. Part I. The sorption of iodine by carbons prepared from carbohydrates." By J. B. Firth.

"Ring-chain tautomerism. Part IV. The effect of the methyl ethyl grouping on the carbon tetrahedral angle." By B. Singh and J. F. Thorpe.

"The transition from the colloidal to the crystalloidal state. Part I. Solutions of potassium oleate." By L. L. Bircumshaw.

"Investigations on the dependence of rotatory power on chemical constitution. Part XVIII. The di-*l*-menthyl